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JUKKA PORANEN

BIOGAS PRODUCTION AND STRUVITE PRECIPITATION FROM SWINE MANURE SLUDGE

Master of Science Thesis

Examiner: prof. Jukka Rintala
Examiner: PhD. Pritha Chatterjee
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ABSTRACT

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Anaerobic digestion of organic wastes is effective technique to produce biogas for energy production. Process also produces digestate, which is rich in phosphorus and nitrogen. Digestate nutrients can be precipitated into struvite crystals. Struvite contains equally portions of magnesium, ammonium and phosphate. Struvite is valuable and efficient fertilizer for agriculture. Study researched anaerobic digestion of swine manure sludge and struvite precipitation from produced digestion effluent. Digestate was used for struvite precipitation experiments, which were optimal precipitation pH, magnesium substrate type, acid treatment method, and precipitation with raw swine manure. Optimal precipitation for phosphorus removal pH was found to be in range 9.5-10.5. Only small difference in phosphorus removal efficiencies between $MgCl_2$ and $MgSO_4$ were found. Without magnesium addition removal efficiency decreased from 92% to 50% in pH 10. Acid treatment of digestate releases phosphorus and cations for precipitation. About 93% of phosphorus is in solids and are available in soluble form after acid treatment. Raw swine manure precipitation had phosphorus removal efficiencies of 80% and 98% in pH levels 7 and 10. Struvite precipitation was found to be economical viable in terms of chemical costs, if inexpensive chemicals for magnesium addition and pH control are available.

TIIVISTELMÄ

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Orgaanisten jätteiden anaerobinen mädätys on tehokas keino tuottaa biokaasua energian tuotantoon. Prosessi tuottaa myös mädätettä, joka sisältää paljon fosforia ja typpeä. Mädätteen ravinteita voidaan saostaa struviittikiteiksi. Struviitti sisältää yhtä suuren määrän magnesiumia, ammoniumia, ja fosfaattia. Struviitti on arvokas ja tehokas lannoite maataloudelle. Tutkimus tutki sian lietteen anaerobista mädätystä ja struviitin saostusta tuotetusta mädätteestä. Mädätettä käytettiin struviitin saostuskokeissa, jotka olivat optimaalinen saostus pH, magnesiumlähteet, happokäsittelytekniikka, ja struviitin saostus sian lietteestä. Optimaalinen poistotehokkuus havaittiin olevan pH alueella 9,5-10,5. Vain pieniä eroja löydettiin fosforin poistotehokkuudessa magnesium lähteiden $MgCl_2$ ja $MgSO_4$ välillä. Ilman magnesiumin lisäystä fosforin poistotehokkuus tippui 92%:ta 50%:iin kun pH oli 10. Mädätteen happokäsittely vapautti runsaasti fosforia ja kationeita saostusta varten. Noin 93% fosforista on sitoutunut kiintoainekseen ja on hyödynnettävissä happokäsittelyn jälkeen. Sian lietteen saostus saavutti 80% ja 98% fosforin poistotehokkuuden pH:n arvoilla 7 ja 10. Struviitin saostamisen löydettiin olevan taloudellisesti kannattavaa, jos edullisia kemikaaleja magnesiumin lisäykseen ja pH:n säätelyyn voidaan käyttää.

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LIST OF SYMBOLS AND ABBREVIATIONS

AD	Anaerobic digestion
COD	Chemical oxygen demand
GHG	Greenhouse gas
HRT	Hydraulic retention time
LCFA	Long chain fatty acid
MAP	Magnesium ammonium phosphate
SEM	Scanning electron microscope
TS	Total solids
VFA	Volatile fatty acid
VS	Volatile solids
WWTP	Wastewater treatment plant

1. INTRODUCTION

Increasing world population and wealth will increase need for livestock and energy production. World total population has increased from 3 billion in 1961 to 7.4 billion in 2016. (FAO, 2018) Production of swine has reached almost 1 billion in 2016 compared to 400 million in year 1961 (FAO, 2018). Increasing livestock production will increase need for fertilizers, especially phosphorus. World's use of phosphate fertilizers (as P2O5) has increased from 34.6 tonnes in 2002 to 48.6 tonnes in year 2016 (FAO, 2018). Phosphorus mining is expected to increase steady level about 2.5-3% yearly and reserves should last about 100 years (Gilbert, 2009). Increasing livestock production has also increased manure production and therefore greenhouse gas (GHG) emissions. Carbon dioxide equivalent emissions from applying livestock manure to soils, which consist indirect and direct nitrous oxide (N_2O) emissions from applied manure, reached 191 Gg in 2016 from 128 Gg in year 1961 and are expected to grow (FAO, 2018). It has been estimated that food and livestock production has to be doubled in year 2050 (Gilbert, 2009). Rising population drives need for increasing energy demand and it reached an estimated 14050 Mtoe (million tonnes of oil equivalent) in 2017, from 10035 Mtoe in 2000 (IEA, 2018).

Phosphorus is essential element for plant and animal growth. Agriculture uses most of the phosphorus as fertilizer, but it is used in other industrial products. Excessive use of phosphorus can lead to decreasing water quality, eutrophication and loss of biodiversity. Most of the chemical fertilizers are produced from phosphate ores, which are located only few places on earth and are finite resource. Europe is highly depended on imported phosphate ore and fertilizer products, because it doesn't have significant phosphate reserves. Population increase and urbanization, as well as changes in diets and consumption are increasing phosphorus demand. Agricultural production will need to meet the increasing demand of food, which have led to increased use of phosphorus as fertilizer in world wide. Increasing demand has pushed world governments and industries to find ways to capture and recycle phosphorus from wastes and reduce dependency on phosphate ore. (Schoumans et al. 2015)

Degradation of organic matter in anaerobic conditions (without oxygen) results to production of biogas by micro-organisms. Anaerobic digestion (AD) converts organic waste material to renewable methane-rich biogas which can be used to produce heat, electricity and vehicle fuel. Leftovers from digestion process are liquid nutrient rich phase and pathogen free solid digestate phase, which can be used as fertilizers in agriculture. AD of wastes decreases pollution, emissions from natural degradation and removes pathogens (Gerardi, 2003). Also digestion reduces costs of waste handling and

provides additional income from these products to waste producers and handlers, such as waste water treatment plants (WWTP) and farms. (Kiran et al. 2016) Anaerobic digestion is one of the techniques to increase renewable energy production and reach 80-95% GHG emission reduction goal in 2050 and achieve sustainable use of renewable resources by European Union (Scarlat et al. 2018). Biogas production has increased significantly from 2.5 billion m^3 in year 2000 to 18 billion m^3 methane equivalent in year 2015 (Eurostat, 2017).) Anaerobic digestion effluents are phosphorus and nitrogen rich and therefore potential feedstock for chemical removal of nutrients by precipitation techniques (Le Corre et al. 2009).

Conventional ways to treat and lower wastes and wastewaters nitrogen and phosphorus concentrations are usually difficult to implement and produce no usable side products. In the recent years, more research have been done to use struvite ($MgNH_4PO_4 \cdot H_2O$) precipitation as a way to remove and recover ammonium nitrogen (NH_4^+-N) and phosphate phosphorus (PO_4^{3-}P) from various types of materials, such as livestock manure and anaerobic digestion effluents (Le Corre et al. 2009). Struvite precipitation process is described as effective, easily implemented and high-yield physicochemical treatment for removing nutrient components (Yetilmezsoy et al. 2017). Struvite precipitation can be used for controlling wastewater nutrient content and avoid excess use nutrients in agriculture and pollution of surface waters. Struvite precipitation creates struvite crystals which are suitable for agricultural fertilizers. Struvite fertilizer has been found to be slow nutrient release and efficient for phosphorus fertilization. (Munch & Barr, 2001) Struvite precipitation from agricultural and digestion process waste waters could create new income for farms and anaerobic digestion plants as sellable fertilizer. Also struvite fertilizer production will decrease need of mining phosphate rock and production of ammonium for fertilizers, therefore decreasing carbon dioxide emissions from conventional fertilizer production. Struvite fertilizers also recirculate phosphorus and decrease need for use of depleting phosphorus reserves. (Massey et al. 2009) Struvite fertilizer can be economical viable and profitable product if demand and price are high enough (Yetilmezsoy et al. 2017).

The objective of the study was producing anaerobic digitate from swine manure sludge and experiment struvite precipitation using produced anaerobic digestate. AD of swine manure sludge was done according typical biogas plant digestion conditions. AD process was monitored and controlled to ensure digestate effluent quality for struvite precipitation.

Second part was conducting struvite precipitation experiments. Objectives of these experiments were finding optimal pH for precipitation, comparing $MgCl_2$ and $MgSO_4$ as magnesium substrates, test precipitation with raw swine manure and acid treatment method. Also researching precipitated crystals and economics of struvite precipitation were studied.

2. ANAEROBIC DIGESTION

AD is a biochemical process which is controlled by group of several micro-organisms. Micro-organisms metabolize organic compounds into gas mixture, and it contains mainly methane and carbon dioxide. Process can happen when conditions are anaerobic or without presence of oxygen. AD is widely used technique to process organic material such as manure and other agricultural waste, municipal solid waste, sewage sludge or lignocellulosic biomass. AD process is used in WWTP and farms to convert waste sludge to biogas and generate income (Figure 1), which would be otherwise incinerated and increase costs for treatment plant. (Weiland, 2010)

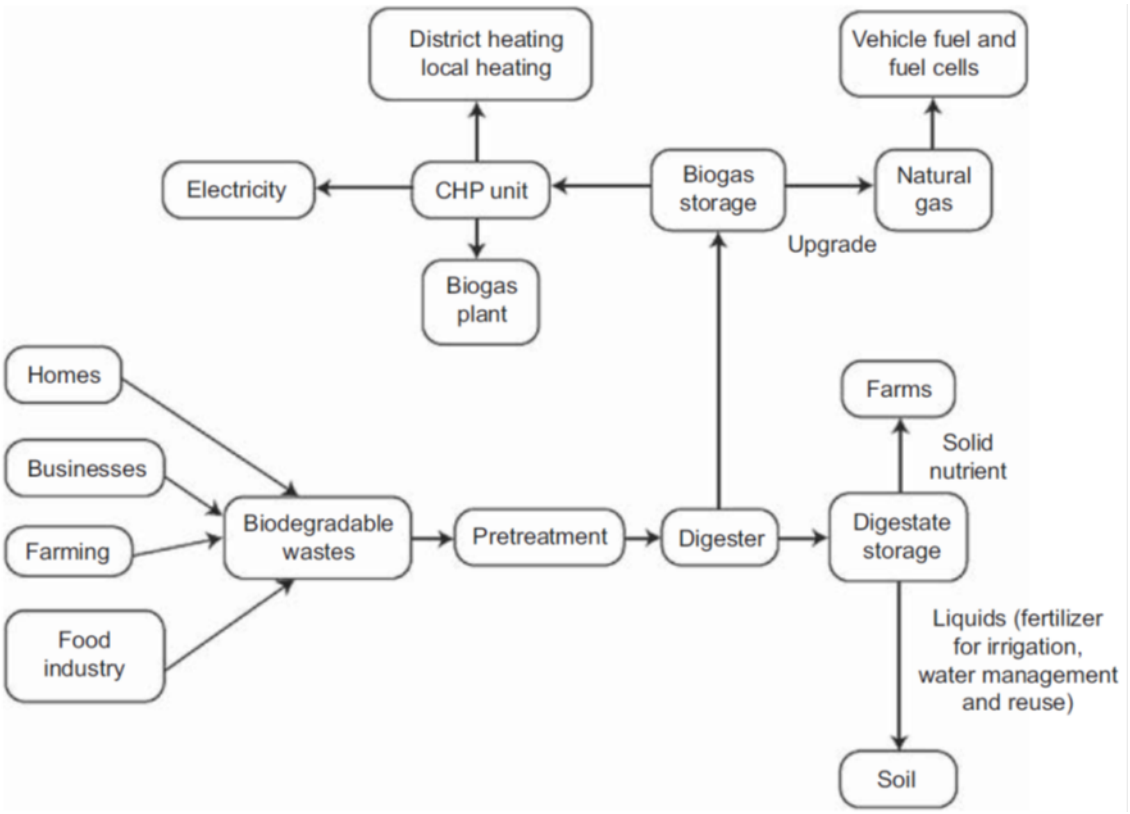


Figure 1. *AD process and utilization of products. (Kiran et al. 2016)*

Biogas contains methane which can be cleaned from other components and to be supplied into natural gas networks. It is also possible to use biogas directly for production of electricity, heat and transportation fuel. Digestate can be used for fertilizer or soil conditioner. AD process offers also other benefits, such as reducing GHG emissions, stabilizing and control waste production, reducing air and water pollution, preventing acidification of biomass, and reducing pathogens in the digestate. (Cuellar & Webber, 2008) These benefits explain why interest in AD process has increased in

recent years many countries and is supported by legislation. In the European Union, it has been estimated that at least 25% of bioenergy is produced from biogas by 2020. (Holm-Nielsen et al. 2008) Electricity produced from biogas could be 63.3 TWh in 2020 in Europen Union (Wellinger, 2011).

AD research has increasing interest to improve the efficiency of the digestion process. Most of the research is done to investigate the AD process to optimize the digester design, operation parameters and the substrate types. (Parawira et al. 2005; Palatsi et al. 2009; Kiran et al. 2016) Digestion process micro-organisms are typically sensitive to changes of operation parameters, such as pH, temperature and organic loading rate etc. To prevent process instability, digestion process is monitored and controlled continuously. Metabolic activity affecting components, such as volatile fatty acids (VFA) and ammonia are important to monitor and control to prevent inhibition of the digestion. Feedstock characteristics are also important, because some feedstock are difficult for AD and other are optimal for the digestion. Difficult feedstocks can be processed with pretreatment or co-digestion. Well balanced digestion medium is one of the corner stones for successful AD process. (Li et al. 2009)

2.1 Process principles

AD is a complex process influenced by several anaerobic micro-organisms, which all have different characteristics and sensitivity to conditions, such as temperature, pH, and metabolites. Digestion process consist several steps (Figure 2). (Kiran et al. 2016)

In AD process, organic matter is broken down into large polymers such as, lipids, carbohydrates and proteins. Disintegration process includes other steps, like phase separation enzymatic decay, and breakdown of the molecules. (Batstone et al. 2002) Organic polymers (proteins, lipids, and carbohydrates) are hydrolysed to monomers, amino acids, lipids and sugars, by enzymes extracted from the cells. Breakdown helps nutrient transport to the cells. Hydrolysis rate can be increased by pre-treating the feed, which makes complex substrates more accessible to micro-organisms and enzymes. (Kiran et al. 2016)

Acidogenesis step includes acidogenic organisms which are able to hydrolyze simple monomers and monomer consisting oligomers into short-chain fatty acids, dicarboxylic acids, carbon dioxide, hydrogen molecules and other compounds. Acidogenesis creates large amounts of hydrogen and CO_2. Production of hydrogen is high when carbohydrate content is high and it can be used for utilized and used for biohydrogen production. (Kiran et al. 2016) Acidogenic bacteria can tolerate low pH levels (5-6) and they have typically high growth rate. Rapid growth of acidogenic bacteria can decrease medium pH level and in inhibit the digestion process. Acetogenic bacteria process and metabolize acidogenic products which are acidic and can cause inhibition when cumulated. (Batstone et al. 2002; Gerardi, 2003)

Acetogenic bacteria process organic molecules to carbon dioxide, acetate and hydrogen in acidogenesis step, which can inhibit methanogenic step if the produced hydrogen molecules aren't metabolized fast enough in the methanogenesis step later. (Batstone et al. 2002) Acetate production is accomplished by acetogenic and acetate-forming bacteria. (Gerardi, 2003)

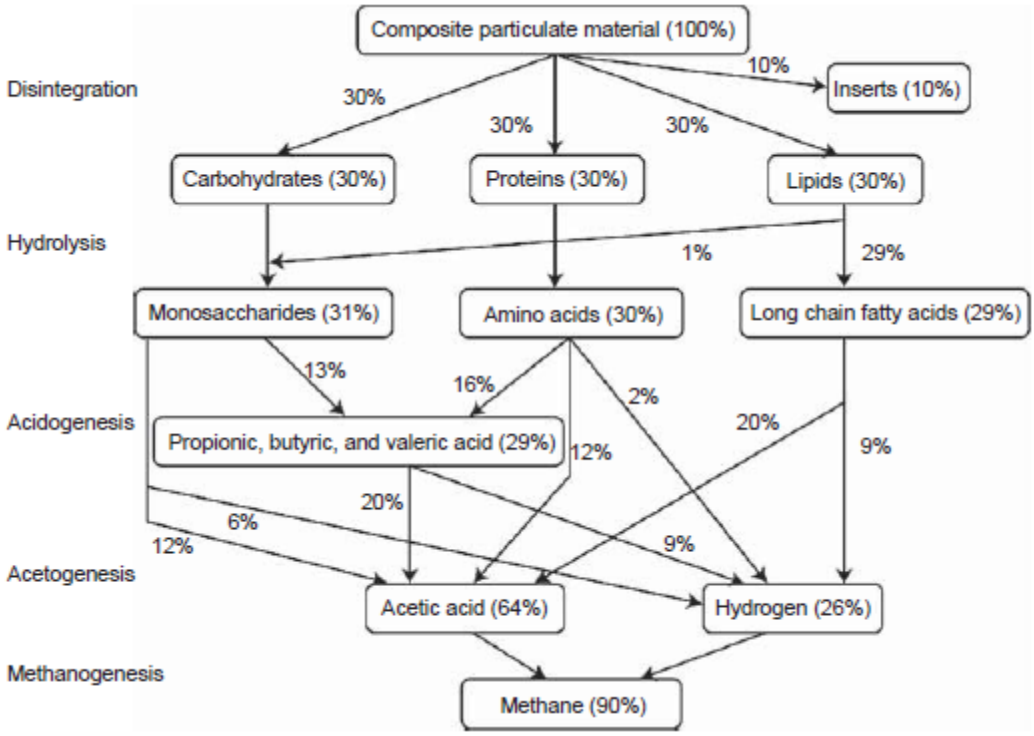


Figure 2. *Anaerobic digestion pathways and steps. Percentages are material mass. (Batstone et al. 2002)*

Methanogenesis step produces the desired end product methane. There are two main micro-organism groups which produce methane from two different substrates. The first group of micro-organisms is acetoclastic methanogens which use acetic acid and are slow-growing. Acetolastic methanogens are sensitive to growing conditions. Second group of methanogenesis are hydrogen-utilizing methanogens. These organisms utilize carbon dioxide and hydrogen to form methane. Oxidation state of the organic carbon is important for methanogenesis. Highly reduced substrate produces more methane. (Batstone et al. 2002)

2.2 Factors affecting the anaerobic digestion process

AD consists several types of micro-organism groups. These groups grow syntrophically benefitting from other micro-organisms and giving different responses to environmental changes. When one group activity is affected or repressed, other groups can be affected too, which can cause lower efficiency or even failure of the digestion process. Most

important factors affecting digestion process are temperature, pH, free ammonia, VFA's and feedstock composition. (Gerardi, 2003)

One of the key parameters for digestion is temperature. Temperature influences in microbial growth, substrate digestion rate and enzyme activity and affect therefore to the methane yield. Conventional AD is usually temperature range of 35-37°C in the mesophilic range (Forster-Carneiro et al. 2008). Thermophilic (50-56°C) digestion has better growth rate, higher load-bearing capacity, faster metabolism, and therefore usually better methane production rate. However, AD process can be respond negatively if the operation temperature isn't relatively constant throughout the process. Mesophilic digestion is more stable and less sensitive than thermophilic digestion. Thermophilic micro-organisms take more time to adapt to the new temperature and have usually lower diversity than mesophilic micro-organisms. Thermophilic process has also higher risk for acidification and it could be caused by the feedstock when it contains too much protein. Acidification can cause inhibition of the process, but problem can be solved by adjusting of the inoculum to the environment. (Kim et al. 2011)

Methanogenesis usually occurs in the pH level range of 6 and 8.5 and have optimal pH range of 7.0-8.0. AD process affected negatively or inhibited when pH level decreases below 6.0 or get higher than 8.5 level. (Gerardi, 2003) Conversion of the proteins and lipids usually creates imbalances in the digestion process and it can accumulate free ammonia and VFA, which could change pH and inhibit the process by affecting extracellular enzymes and the hydrolysis process. Accumulation of VFA decreases pH and inhibit methanogenesis. (Kiran et al. 2016)

Free ammonia inhibits methane producing enzymes (Gerardi, 2003). Ammonia can cause proton imbalances and potassium deficiency which can lead to cell lysis. High ammonia concentration cause inhibition but certain inhibition concentration level is undefined and it can range from 650-4000 mg/L. (Mata-Alvarez 2003; Hartmann & Ahring 2005; Angelidaki et al. 2005) Although high ammonia can cause operational difficulties for anaerobic digestion process, it has been reported that process organisms can adapt to the high concentrations of free ammonia when other parameters are stable. (Banks et al. 2011) Excess ammonia can be removed with different techniques, such as ammonia stripping, biological removal processes and electrochemical technique of converting ammonia. (Kiran et al. 2016) Free ammonia is usually considered as a difficulty, but in some cases high ammonia can stabilize biogas production by balancing against VFA accumulation pH level decrease (Banks et al. 2011).

Micro-organisms of the AD metabolize different organic compounds, such as proteins, lipids and carbohydrates. Biogas content is affected by biomass composition. Carbon oxidative state found in the feedstock can determine methane content, because more reduced carbon creates more methane. (Kiran et al. 2016) Also feedstock biomass carbon/nitrogen ratio should be well balanced for optimal biogas production. Ideal ratio

of C/N should be between 20 and 30 for digestion process. In many cases feedstock C/N ratio isn't optimal for digestion and co-digestion with balancing feedstock is usually applied. (Gomez et al. 2005)

Lipid concentration of the feedstock biomass is important for digestion process. High lipid content can inhibit the digestion process. Methane potential of the lipids are high compared to carbohydrates, but long chain fatty acids (LCFA) are inhibitory for the AD in high concentrations and could cause failure of the system. LCFA could prevent cell transport mechanisms of the micro-organisms, because LFCA are absorbed to the cell surfaces. Also they can cause microbial flocs absorbing to the material. (Zonta et al. 2013) High LCFA concentration can be handled with dilution or co-digestion with low-lipid feedstock, such as cattle manure (Palatsi et al. 2009).

Micronutrients are crucial for digestion process. Magnesium, phosphorus and potassium are the most important micronutrients for activation and functioning digestion organisms. With micronutrients, other nutrients are also needed for enzymatic activity and cell growth. Nickel is important for coenzymes, iron for electron carriers, cobalt is needed for vitamins, calcium stabilize the cellular walls and is needed for thermal stability and zinc is needed for production of different enzymes. However, all micronutrients are toxic in high enough concentrations. Insufficient nutrients can be supplemented to the AD process and excess nutrient concentrations can be diluted by co-digestion. (Chen et al. 2008)

2.3 Anaerobic digestion systems characteristics

AD systems can be characterized by different parameters. These parameters can be temperature of the operation, solid content of the digesting mixture, number of reactors, operation type, and size of the reactor system.

Temperature decides how digester operates and what organisms are present in the digestion. Digesters usually operates in two temperature ranges, either mesophilic at 35-40°C or thermophilic at 50-60°C. Mesophilic digestion temperature is usually applied for animal manure and agricultural/industrial organic wastes. Thermophilic digestion temperature is used for sanitation for pathogen rich feedstocks and need for faster retention time. (Gerardi, 2003) Psychrophilic temperatures (<20°C) can be used for lagoon digestion with long retention time (Lettinga et al. 2001).

Solid content of the digestion mixture is important for choosing digester type. Low solid content (less than 3-4%) is usually treated in single-phase liquid system. Wet solids (solids 12-15% or more) are treated usually with mixed reactors as slurry. Dry solids are treated usually in plug-flow reactors. (Kiran et al. 2016)

The AD system can be assembled as single reactor or combination of several reactors, different or similar type. Usually when digesting solids or slurry feedstocks more than one reactor is being used. Operation conditions determine how many reactors are used as stages for digestion. Usually first stage is used for breaking the substrate in hydrolysis step and form acids. Second stage is usually for methanogenesis. Multi stage system has an advantage being more stable than one stage AD systems. Leachate can be recirculated to maximize biogas output. Also different stages can be operated in two different temperatures to optimize process. (Gerardi, 2003)

Digestion system can be continuous or batch type operation. Continuous reactor is fed continuously during the process and it will keep producing biogas as long as it is loaded. Batch type reactors are loaded at the beginning of the process and emptied when biogas yield has decreased. Some of the material is left (10-15%) to the reactor as a seed for the next cycle in batch type system. (Gerardi, 2003)

Reactors can be characterized as their size. Small scale reactors have been used in farms and biogas produces locally in the site and residues of the digestion process can be used in the farm. Large scale reactors are used to process mixture of feedstocks. Both of the sizes can have heating and mixing, as well as continuous or batch type. Large scale systems are usually more profitable and can handle different feedstock. Both types usually operate in mesophilic temperature. (Kiran et al. 2016)

2.4 Monitoring and controlling

Monitoring and controlling digestion are used to measure performance and take needed action for the process. Various methods have been developed to monitor AD process (Table 1). Monitoring and controlling the AD process prevents upcoming instabilities before process failure, improve the digestion process and to perform successful start-up. (Gerardi, 2003) First it is needed to define the control objective, which i.e. pH stabilization and optimization. After definition, suitable measurements are being selected. (Kiran et al. 2016)

Monitoring pH is done because pH affects activity of the micro-organisms. Measuring pH level tells changes in acid and base concentrations. However, it cannot be the only parameter to evaluate the state of the systems, because pH level is influenced by buffer capacity of the medium, which is usually affected by carbonates, ammonium/ammonia and VFA's. (Gerardi, 2003)

Alkalinity is measured to evaluate buffer capacity of the system. Alkalinity of the system is measured as total- and bicarbonate alkalinity. Total alkalinity can be measured by titration to pH 3.7 and is expressed as capacity of system to maintain pH level when system is challenged by pH decrease by acids. Increasing VFA will increase total alkalinity. Therefore bicarbonate alkalinity is measured by titration to pH 5.75, which can reflect the buffer capacity of the system. Various methods have been developed to measure bicarbonate alkalinity. (Kiran et al. 2016)

Organic matter is measured as total solids (TS), volatile solids (VS), chemical oxygen demand (COD), total organic matter and biological oxygen demand, which tells difference between influent and effluent in organic matter. (Forster-Carneiro et al. 2008)

Biogas production rate is the one of the most used measurements to evaluate process stability. Decrease in the biogas production can suggest that VFA's are being accumulated in the reactor as a result of overloading or increased concentration of inhibitory substances. Production rate cannot be used as early warning, because it isn't sensitive enough. (Gerardi, 2003)

Biogas composition usually consists of carbon dioxide and methane. Increased carbon dioxide level relatively to methane level can tell imbalances in the process, but isn't an early indicator. Carbon dioxide level is affected by alkalinity of the medium and pH level in the reactor, so carbon dioxide level change doesn't necessary indicate instable process. (Ryhiner et al. 1992) Hydrogen is another significant compound. Acetogens performance is regulated by hydrogen concentration and is used detection the imbalances of digestion process. (Molina et al. 2009) Measuring hydrogen form the gas phase doesn't corresponds with the actual concentration affecting micro-organisms in

the aqueous phase, and therefore measuring dissolved hydrogen is more reliable measurement (Frigon & Guiot, 1995).

Table 1. *Methods used for monitoring anaerobic digestion parameters. (Kiran et al. 2016)*

Parameter	Method
Alkalinity	Titration Spectrophotmetry
Total, volatile solids	Drying
Chemical oxygen demand	Oxidation and spectrometry
Total organic carbon	Infared analyzer
Biochemical oxygen demand	Bioassay
Biogasflow	Volumteric displacement Manometric
Methane	Gas chromatography Infared analyzer Biogas treatment with lime Chamical sensors
Hydrogen	Mercury-mercuric oxide detector cell Exhaled hydrogen monitor Palladium metal oxide semiconductors Thermistor thermal conductivity
Dissolved hydrogen	Amperomteric probe Hydrogen/air fuel cell Mass spectrometry Silicon or Teflon membrane tubing transfer
VFAs	Gas chromatography (offline and online) Gas extraction at pH < 2 Indirectly via titration Fluorescence spectroscopy Near-infared spectroscopy

VFA's are intermediates to measure in anaerobic digestion process. VFA accumulation leads to pH decrease and stressing methanogens. The acetate concentration increase doesn't tell necessarily process imbalance if the biogas production has also increased. Propionate and butyrate accumulation are usually signs of change in process stability since they happen when hydrogen concentration increases. Propionate is usually accumulated first, because it needs six times less concentrated hydrogen than butyrate. Characteristic of propionate is good indicator for imbalance with butyrate. However, no safe levels of VFA's are determined for stable process because other variables affect the AD process. (Boe et al. 2008)

VFA concentrations are usually detected by gas chromatograph. Analysis requires usually sample preparation and sampling. Gas chromatograph measurement requires also complex analytical systems and equipment, with trained users. VFA's can measured also by spectroscopy, electrochemically or mass spectrometry and titration method. Taking representative sample is difficult and errors can be high, because AD medium heterogeneous and viscous characteristic. Online systems could prevent these types of errors and predicting process failure would be easier. However, online measurements are challenging because sample preparation and sensor fouling, which make most of the online measurement unreliable. (Holm-Nielsen et al. 2008)

Measuring metabolic activity can be other parameter to monitor process stability and success. The microbial activity can be measured and evaluated by specific methanogenic activity, molecular techniques such as DNA/RNA probing and detecting metabolic components i.e. enzymes, ATP and phospholipids. These measurements are however often time consuming or need low solid content, but can give better understanding to the system. (Kiran et al. 2016)

Anaerobic digestion system can be controlled when process instability is detected by manipulating variables. Hydraulic retention time (HRT) is the most used one. Retention time should high enough to for the slowest-growing micro-organisms to prevent wash out of organisms. These reactors have same retention time for biomass and the feedstock. Sludge can be recirculated to increase biomass concentration. HRT manipulation is often limited with waste storage capacity. Thermophilic conditions have retention time of 4-6 days and mesophilic 10-15 or longer if stable operation is desired. (Pind et al. 2001) In codigestion, the mixture ratio of the feedstock can be manipulated to eliminate nutrient deficiency, dilute inhibitory substances and enhance the process. (Li et al. 2009) Other controllable parameters are acid, base and carbonate addition to control pH level of the reactor or the feedstock. However, these methods can raise costs and be inefficient. (Pind et al. 2001)

2.5 Biogas utilization and purification

Biogas mainly contains methane and carbon dioxide, while smaller concentration components are hydrogen sulphide, ammonia hydrogen, nitrogen, carbon monoxide halogenated carbohydrates and oxygen. Biogas consists also water as a vapour and may also contain small particles. Energy content of the biogas is determined by methane content of the biogas. (Gerardi, 2003)

Biogas can be used in various applications. Gas is utilized electricity production in small scale in farms and larger scale in power plants. Biogas can be used for heating and is used for combined heat and power plants. Biogas can be fed to the natural gas pipeline system, but it will need purification to remove carbon dioxide and other

components. Hydrogen sulfide removal is the most important, because it causes corrosion in the pipelines. (Kiran et al. 2016)

Hydrogen sulfide can react most of the metals and is reactive in high pressure and temperature. Hydrogen sulfide can be removed in the digestion process by supplying small amounts of oxygen to the reactor to activate sulfide oxidizing organisms. Organisms converts sulfide to elemental sulfur and also sulfate. Sulfide can be removed by water scrubbing or iron-containing compounds, such as iron chloride or iron oxide. Humidity also has to be removed, because it causes formation of sulfur oxidation. Water is removed usually by condensation method. Solid particles can be removed by membranes or activated carbon. Excess carbon dioxide is removed to meet the standards for vehicle fuel and natural gas pipelines. Carbon dioxide removal can be done by variety of ways, but most used ones are water adsorption, carbon sieves and membrane separation. Oxygen and other compounds are removed with previous compounds or using specific techniques. (Kiran et al. 2016)

2.6 Anaerobic digestion of swine manure

Swine manure is excellent feedstock material for AD due to its buffering capacity and high concentration of nutrients needed for the anaerobic micro-organisms (Regueiro et al. 2012). Swine manure contains usually high concentrations of VS, fats, degradable dissolved organic matter and has high C/N ratio. Swine manure has relatively low biogas yield 20-30 m^3/ton when compared to other animal manures. (Angelidaki & Ellegaard, 2003) Swine manure has also high ammonium concentration about 2-3 g N-NH_4^+ /L, which could cause inhibition during digestion. Swine manure is usually co-digested with high carbon content feedstocks to improve C/N ratio and biogas yield. (Hartman & Ahring, 2006) Co-digestion enhances biogas production and is used for swine manures. Animal manures are digested usually in continuously stirred reactors at mesophilic temperature. (Weiland, 2010).

AD of animal manures has been promoted to decrease emissions of methane during manure storage (Novak & Fiorelli, 2010). AD of swine manure offers both treatment and production of renewable energy. Biogas reduces GHG emissions due to the replacement of fossil fuels, reduced fertilizer production and from manure management. AD of livestock manure helps farms to reduce costs and make possible to earn by energy production. (Kaparaju & Rintala, 2011)

3. STRUVITE

Struvite is a phosphate containing magnesium, ammonium and phosphate in equal molar concentrations. The general formula for struvite minerals is

$$AMPO_4 \cdot 6H_2O \quad (1)$$

where A is ammonium (NH_4^+) or potassium (K), M is magnesium (Mg), cobalt (Co) or nickel (Ni) (Le Corre et al. 2009) Struvite form crystallises as orthorhombic structure. Main physical and chemical properties of the struvite are summarized in Table 2.

Table 2. *Chemical and physical properties of struvite.(Le Corre et al. 2009)*

Chemical nature	Mineral salt
Chemical name	Magnesium ammonium phosphate hexahydrate
Chemical formula	$MgNH_4PO_4 \cdot 6H_2O$
Aspect	In pure form white, but also other colours as unpure
Structure	Orthorhombic regular PO_4^{3-} octohedra, distorted $Mg(H_2O)_6^{2+}$ octohedral, and NH_4 groups hold together by hydrogen bonding, (Abbona and Boistelle, 1985).
Molecular weight	245.43 g mol^{-1}
Specific density	1.711 g cm^{-3}, (Borgerding, 1972)
Solubility	Low in water: 0.18g l^{-1} at 25°C in water High in acids: 0.33g l^{-1} at 25°C in 0.001 N HCl; 1.78g l^{-1} at 25 °C in 0.01 N HCl (Bridger et al., 1961).
Solubility constant	$10^{-13.26}$ (Ohlinger et al. 1999)

Struvite occurs in various biological mediums. Struvite has been found in different organic materials such as deposits of guano and animal manure, where it is produced through the microbial combination of NH_4^+ ions from bacterial metabolism with present magnesium and phosphates. (Le Corre et al. 2009) Struvite can be also found in human kidneys as calculi and urinal stones (Ronteltap et al. 2007).

Struvite precipitated scale deposits can cause problems to waste water treatment plants and digestion systems (Doyle et al. 2003) Spontaneous scale of struvite is common. Struvite usually scale on high turbulent places i.e. valves, propellers, pumps and elbows and in parts where phosphates have high concentration. Scaling often increases need of maintenance and decreases efficiency of the process. Struvite scaling is usually removed

by acid treatment. Struvite scaling has been tried to solve with water effluents, preventing with iron salts and adding chemical inhibitors. (Le Corre et al. 2009)

AD digestates and agro-industrial wastes contains high concentrations of soluble phosphates (PO_4^{3-}) and ammonium (NH_4^+) which can be precipitated as struvite ($MgNH_4PO_4 \cdot 6H_2O$) and recovered as crystallized product. (Le Corre et al. 2009) Struvite produced from waste has low content of heavy metals and pathogenic contaminants (Uysal et al. 2010). Struvite has also high nutrient value per unit weight compared to e.g. manure. Struvite is more usable and effective fertilizer compared to mineral phosphates in wide range of soil pH levels. Struvite precipitation has potential to produce high quality fertilizer from side streams and reduce maintenance costs for waste treatment. (Massey et al. 2009)

3.1 Struvite formation

Struvite can form rather large crystals and therefore struvite formation is usually preferred over other crystals formation such as calcium- and magnesium phosphates at right conditions (Schoumans et al. 2017).

Equation for magnesium ammonium phosphate (MAP) ($8.5 < pH < 9.5$):

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O\,(s) + H^+ \quad (2)$$

Equation is considered to be most accurate presentation of struvite precipitation, because it have been noticed that struvite precipitation lowers pH of the solution and therefore it is suggest that HPO_4^{2-} will participate more than only PO_4^{2-} (Schuiling & Andrade, 1999)

Also magnesium potassium phosphate can be formed when enough potassium is present in precipitation. Formation of K-struvite equation ($9 < pH < 10.5$):

$$Mg^{2+} + K^+ + HPO_4^{2-} + 6H_2O \rightarrow MgKPO_4 \cdot 6H_2O + H^+ \quad (3)$$

Low pH conditions make possible for precipitation of magnesium hydrogen phosphate, which doesn't require ammonium or potassium cation. Equation of magnesium hydrogen phosphate ($pH < 8.5$):

$$Mg^{2+} + HPO_4^{2-} + 6H_2O \rightarrow MgHPO_4 \cdot 6H_2O \quad (4)$$

Optimal pH level varies depending on the composition of the solution where struvite is precipitated (Schoumans et al. 2017). Other precipitates are possible in crystallization of struvite (Table 3) when suitable conditions and ions are present in solution (Mohan et al. 2010).

Table 3. *List of the possible precipitates with names and chemical formulas when struvite is precipitated in solution with Mg^{2+} and Ca^{2+}. (Mohan et al. 2010)*

Chemical name/Commercial name/Abbreviation	Chemical formula
Magnesium ammonium phosphate / Struvite	$MgNH_4PO_4.\ 6H_2O$
Magnesium hydrogen phosphate / Newberyite / MHP	$MgHPO_4$
Magnesium phosphate / Bobierrite / MP8	$Mg_3(PO4)_2.\ 8H_2O$
Magnesium phosphate/ Cattiite / MP22	$Mg_3(PO_4)_2.\ 22H_2O$
Hydroxyapatite / HAP	$Ca5(PO_4)_3OH$
Tricalcium phosphate / Whitlockite / TCP	$Ca_3(PO_4)_2$
Monenite / DCP	$CaHPO_4$
Octacalcium phosphate / OCP	$Ca_8(HPO_4)_2(PO_4)_4.\ 5H_2O$
Dicalcium phosphate dehydrate / Brushite / DCPD	$CaHPO_4.2H_2O$
Calcium carbonate / Calcite	$CaCO_3$
Magnesium carbonate / Magnesite	$MgCO_3$
Nesquehonite	$MgCO_3.3H_2O$
Dolomite	$CaMg(CO_3)_2$
Huntite	$CaMg_3(CO_3)_4$
Magnesium hydroxide / Brucite	$Mg(OH)_2$

Conditions of struvite formation in natural or industrial systems, such as wastewater or digestates, have also other ions than those on the struvite (NH_4^+, PO_4^{3-}, Mg^{2+}). Ions can be Fe^{3+}, Fe^{2+}, Ca^{2+}, Na^+,K^+,Cl^-,SO_4^{2-}, CO_3^{2-}, HCO_3^-, as well as other ions, such as organic ions, oxalates and silicates. Other ions presence and concentrations have affect to dynamics of interactions and ion clustering, and changes speciation profiles of hydrogen phosphates (H_3PO_4) and ammonia (NH_3) relation to pH through ionic- and noncovalent interactions, alignment and clustering of different groups (Figure 3). Systems can create favourable environment for struvite precipitation even though the molar rations of concentrations may be different that are in struvite crystals (i.e. MAP have molar ratio 1:1:1). (Tansel et al. 2018)

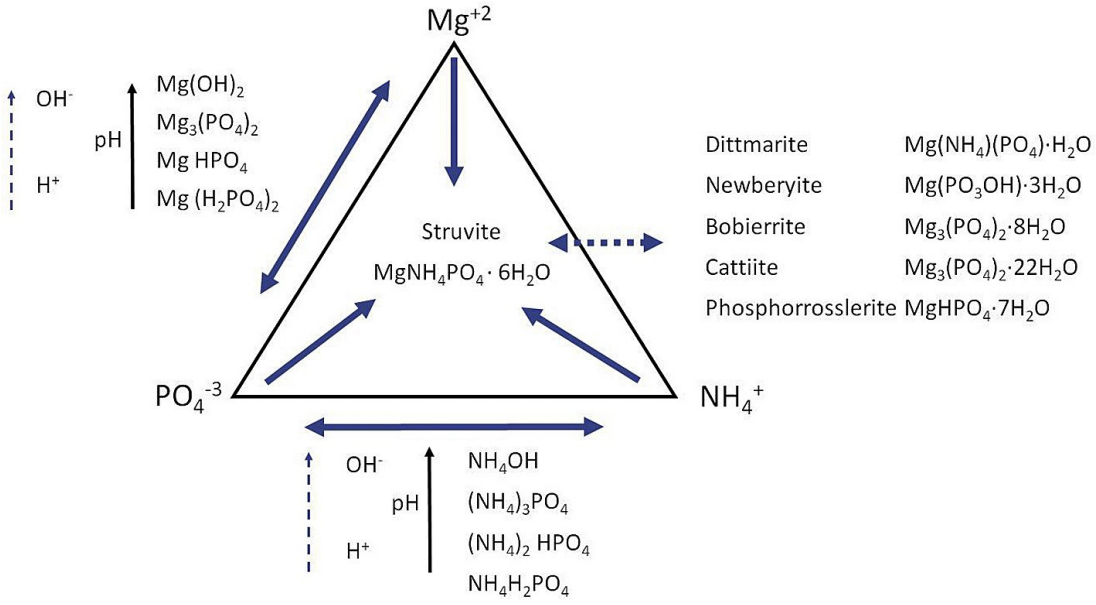


Figure 3. *Interactions of NH_4^+, PO_4^{3-}, and Mg^{2+} ions in present struvite crystal formations. (Tansel et al. 2018)*

Every medium have their own characteristic to precipitate and form struvite crystals. Characteristic varies and determines how much struvite and other precipitants are crystallized and in what molar ratio. (Tansel et al. 2018)

3.2 Crystallization mechanism, crystal structure and morphology of struvite

Crystal formation is complex process which leads to solid phase of regular structures or as crystals. Crystallization is commonly used for industrial applications for separating desired solid phase from the liquid. (Le Corre et al. 2009) Because it's usability, crystallization is highly researched and innovations are made, despite its complex nature (Tansel et al. 2018). Crystal formation mechanism can be divided in two parts, nucleation and crystal growth.

Nucleation process starts the crystal birth into a liquid media. Ions free in the media combines together to form crystal embryos. Embryos are the first state of the crystals. Primary nucleation is birth of the crystalline particles and it can be happen by two different mechanisms. Heterogeneous process occurs due to presence of foreign particles or other impurities and it happens usually in impure solution like wastewaters. Homogenous process happens in highly purified solutions as spontaneously crystallization. Secondary nucleation is induced by same specie crystals. Kinetics of the reaction governs the nucleation process. (Le Corre et al. 2009)

Crystal growth corresponds to the development of the crystals until equilibrium state is reached in the media. Crystal growth happens after nucleation and it determines the final shape and size of the crystals according crystallization kinetics, which is influenced by several factors in the media, such as pH, supersaturation level, thermodynamics and kinetics. (Le Corre et al. 2009)

Struvite forms orthorhombic crystals (Figure 4) Struvite consists of $Mg(6H_2O)^{2+}$ (octohedral), NH_4^+ (tetrahedral), and PO_4^{3-} (tetrahedral) groups. These groups are held together by hydrogen bonds (Figure 4a). The orthorhombic struvite crystals have cell dimensions of a = 6.941 ± 0.002 Å, b = 6.137 ± 0.002 Å, c = 11.199 ± 0.004. Tetrahedron of PO_4^{3-} is regular with bond length of 1.543 Å and the distorted $Mg(6H_2O)^{2+}$ octahedron has bond lengths of 2.0810 Å. Mg-H2O has bond and 0.792 Å for H_2O-H bond. Water molecules form six short hydrogen bonds which are among the shortest found in crystalline hydrates, with lengths ranging from 263.0 pm to 269.5 pm while seventh contact length with another water molecule is longer 314.1 pm. (Tansel et al. 2018) Ammonium ion forms 280 pm long strong bond while other hydrogen bonds are weaker (Stefov et al. 2005). Bond between atoms is stronger when bond length is shorter. Stronger bonds have also higher dissociation enthalpy or needed bong breaking energy.

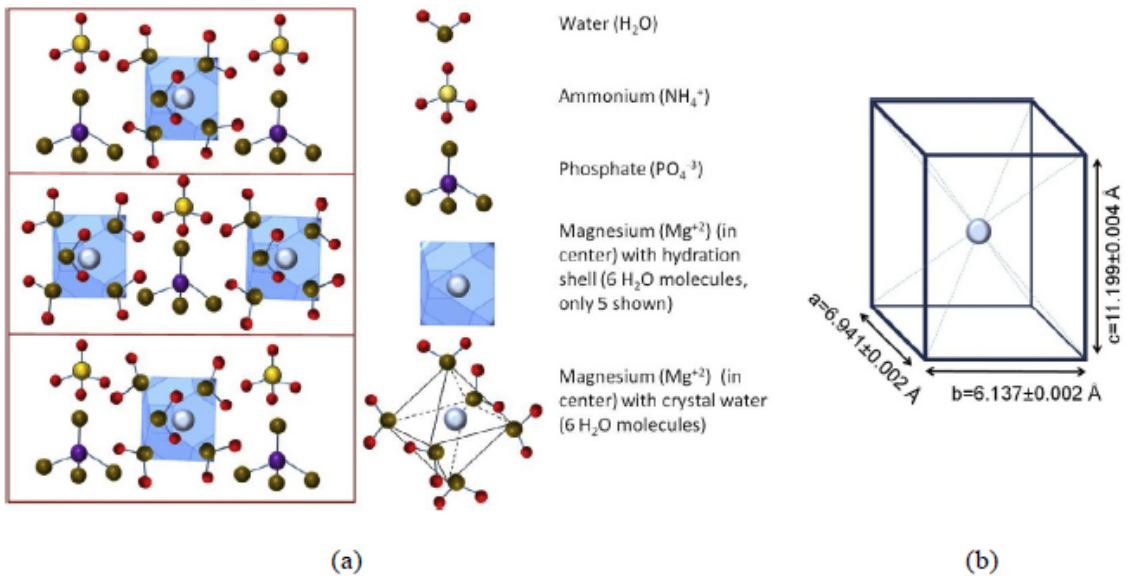
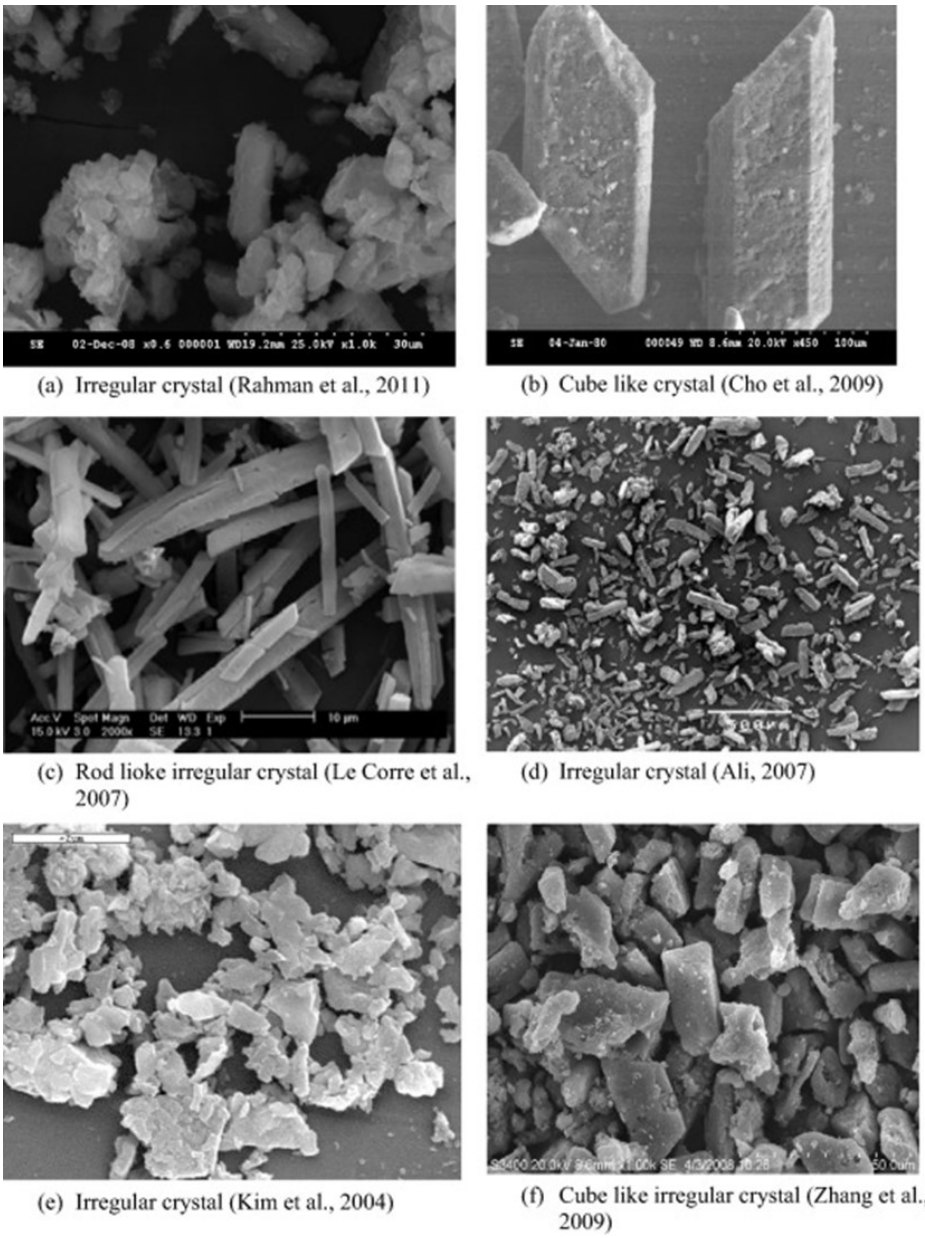


Figure 4. *Struvite crystal structure: (a) ionic group arrangement (b) struvite crystal dimensions. (Tansel et al. 2018)*

Struvite crystals growth may be caused by formation of salt bridges. Salt bridges are a combination of electrostatic interactions and hydrogen bonds. Strength of hydrogen bonds is increased when ions are present, which may be due to salt bridges, and also could explain bio mineralization mechanism of struvite (Urbic, 2004) Controlling

influence of crystallization is considered to be on hydrogen bonds during initiation and growth of the crystals in large complex salts, and it affects on ionic packing and morphology of the crystals. (Xu et al. 2016) Struvite has 10-11 hydrogen bonds and their strength is affected dielectric constant and bond accepting/donating ability. The free energy analysis shows that stable minimum is achieved in six-fold coordination in the octahedral arrangement (Ikeda et al. 2007)

Struvite crystals morphology usually varies depending on the growth parameters i.e. pH, temperature and cation/anion concentrations. The different types of morphologies can be described as (Figure 5) i.e. elongated type, needle type, X-shape, dendritic type or pyramidical type (Prywer et al. 2012). Differences may be caused by ionic and noncovalent interactions, clustering of ions and also rearrangements, which are affected by pH, temperature, residence time and dynamics of ionic interactions. (Tansel et al. 2018)



(a) Irregular crystal (Rahman et al., 2011)

(b) Cube like crystal (Cho et al., 2009)

(c) Rod lioke irregular crystal (Le Corre et al., 2007)

(d) Irregular crystal (Ali, 2007)

(e) Irregular crystal (Kim et al., 2004)

(f) Cube like irregular crystal (Zhang et al., 2009)

Figure 5. *Different struvite crystal structures. Picture references are in original review article. (Rahman et al. 2014)*

Impurities and presence of other ions can cause change in crystal growth patterns (Tansel et al. 2018). Phosphate concentration and retention time have effect on growth rate. Higher concentrations of phosphates increases crystal growth rate. (Abe, 1995) Increasing pH level can make smaller crystals (Kozik et al. 2011). Also nitrogen phosphorus molar ratio has effect on crystal size (Liu & Qu, 2017). Other ions and impurities can block crystal growth sites and prevent struvite formation (Le Corre et al. 2009). Struvite analogues with other than ammonium ion in the structure can influence on crystal growth and shape (Tansel et al. 2018). Nucleation process for crystal formation is induced in supersaturated concentrations (Bouropolous & Koutsoukos, 2000) and foreign particles in the solution (Chen et al. 2010).

3.3 Effects of pH to struvite precipitation

Optimal precipitation pH for struvite is usually in the wide range of pH levels. Typical pH range is 7.0-11.5 for precipitation, but optimal pH ranges from 7.5 to 9.0 (Hao et al. 2008). Struvite solubility decreases with increasing pH, and it is shown that minimum struvite solubility is reached at pH 9.0-10.7 (Doyle & Parsons, 2002). Precipitation of struvite depends on the concentration of magnesium, ammonium and phosphorus. Also other factors, such as pH, temperature, aeration rate play key role in crystallization. Other ions may interfere with struvite formation. Soluble calcium might form phosphate crystals in higher pH levels and lower struvite precipitation. (Stratful et al. 2001; Le Corre et al. 2005; Hao et al. 2008) Several studies have researched the effect of pH on removal efficiency of phosphorus and nitrogen (Ohlinger et al. 1999 & Stratful et al. 2001). These studies have shown that higher pH results more efficient phosphorus and nitrogen removal with varying influents. Rising efficiency on increasing pH might link to decreasing solubility of struvite in higher pH. More than 90% phosphorus removal has been achieved using pH over 8.3 with influent. (Adnan et al. 2003) Good crystallization results have been achieved when pH and other influencing factors have been steady in bench scale (Adnan et al. 2003) and in continues crystallization process (Hutnik et al. 2012 & Matynia et al. 2013). Hao et al. (2013) found out that struvite formation is more likely to happen near neutral pH 7.0-7.5 as pure as 99.7% struvite.

Solution pH have also effect on the growth rate of struvite crystals (Ohlinger et al. 1999) Higher pH causes increase in supersaturation an therefore increase crystal growth rate of struvite (Le Corre et al. 2009). Crystal size and purity is affected by solution pH level. High pH decreases struvite crystals size (Matynia et al. 2006 & Kozik et al. 2011) Purity of the struvite was decreased in higher pH from 30-70% in pH 8.0-9.0 to <30% in pH over 9 (Hao et al. 2013). High pH produce increased nuclei population densities which might cause smaller crystals and also increases size diversity.

3.4 Molar ratio and magnesium substrates in struvite precipitation

Optimal molar ratio for Mg/P is depended on precipitation media and desired phosphorus removal efficiency. Yetilmezsoy & Zengin (2009) concluded that most optimum ratio of for precipitation is 1:1:1 Mg^{2+} : NH^{4+}-N : PO_4^{3-} for pretreated poultry manure wastewater and Zhang et al. (2009) stated best ration to be 1.15:1:1 Mg^{2+} : NH^{4+}-N : PO_4^{3-} for landfill leachate. However, optimal molar ratio is affected by several factors i.e. other soluble ions. More research is needed to find optimum molar ratio for different feedstocks and conditions. (Rahman et al. 2014)

Most of the research on struvite precipitation is done with $MgCl_2$ and others usually with $MgSO_4$, MgO and $Mg(OH)_2$. The use of $MgSO_4$ has no difference on precipitation compared to $MgCl_2$ (Yetilmezsoy & Zengin 2009). Magnesium hydroxide $Mg(OH)_2$ was found to increase total suspended solids (TSS) and have lower ammonium nitrogen removal efficiency, but it increases solution alkalinity and phosphorus removal. (Kim et al. 2007) Producing high purity struvite also requires addition of phosphates with magnesium, because calcium tends to interfere with struvite crystallization in calcium rich wastewaters (Doyle & Parsons 2002).

3.5 Effects of other ions on struvite crystallization

Struvite precipitation is highly effected by the interaction of calcium and magnesium. Relative concentrations of these ions can inhibit struvite precipitation as calcium tends to form calcium phosphates i.e. hydroxylapatite (Doyle & Parsons, 2002 & Le Corre et al. 2005). Presence of calcium and carbonates can lengthen the induction time and affect negatively to growth rate of struvite crystals. Calcium can influence struvite formation by competing for phosphate ions or by interfering with struvite crystallization. (Le Corre et al. 2005 & Song et al. 2007) Co-precipitation of magnesium phosphates is usual in high concentration of carbonates (Doyle & Parsons, 2002 & Ronteltap et al. 2007) Potassium can also inhibit formation of MAP as K-struvite $MgKPO_4$ precipitation (Wilsenach et al. 2007).

Le Corre et al. (2005) researched calcium concentration effects on struvite crystallization. They concluded that calcium have significant effect on struvite precipitation rate, efficiency and crystal formation (Figure 6). Also calcium was shown to compete in precipitation with struvite and form amorphous calcium phosphates.

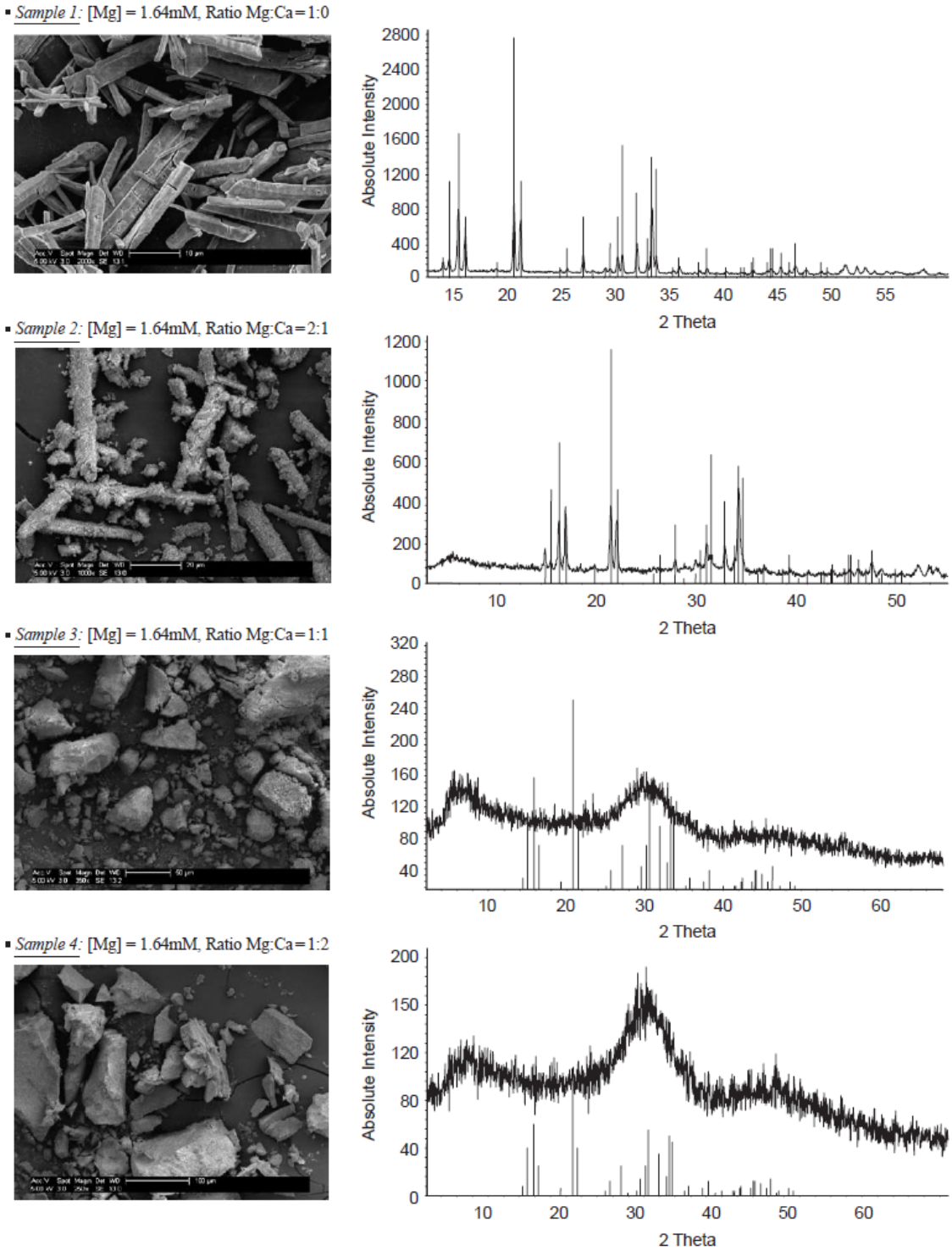


Figure 6. *Calcium effect on struvite crystallization in different Mg/Ca molar ratios. Scanning electron microscope (SEM) pictures with their X-ray analysis. (Le Corre et al. 2005)*

Calcium phosphates is shown to precipitate pH > 9.5 and meanwhile effective struvite precipitation pH is 8.0 level and above. Changing chemical composition of the precipitation solution i.e. increasing magnesium/calcium concentration ratio, more effective struvite formation can be achieved, especially in high pH levels (Doyle & Parsons, 2002)

3.6 Acid treated precipitation

Waste water and their digestate have usually pH between 7 and 8. Phosphorus is in soluble form in the liquid and precipitated as struvite or calcium as dicalcium phosphate. (Bril & Salomons, 1990) Large part of the available phosphates can be released to soluble form by lowering pH of the solution. (Forbes et al. 2008; Masse et al. 2008; Schoumans et al. 2017). Phosphorus bound to organic matter is released by hydrolysis when lowering pH level of the solution. (Chen et al. 2007)

Phosphorus released in soluble form can be separated from solids removing liquid phase and phosphates then can be precipitated by increasing pH and adding magnesium or calcium. (Schoumans et al. 2017) Process produces small volume of concentrated phosphorus rich precipitates, which can be transport or used as secondary resource for fertilizers industry (Ehman et al. 2017) Remaining fraction with low phosphorus concentration can be better applied as fertilizer without exceeding application standards of phosphorus. However, chemical and operating costs should be lower than other uses to be economical option. (Schoumans et al. 2017)

3.7 Struvite as fertilizer and struvite fertilizer production

Struvite has slow nutrient release rate which make it effective and prevents excess solubility and nutrient leaching. Struvite has been tested as fertilizer in several studies. (Bashan & Bashan 2004) Struvite had been commercially produced in different locations (Rahman et al. 2014). Struvite has been found to be useful fertilizer for plants which requires low-soluble and slow-release fertilizer. Slow nutrients release of struvite helps plants to uptake nutrients throughout the growing season and use most of the nutrients when compared to high soluble fertilizers. Struvite fertilization application is also less frequent, when compared to conventional fertilizers. (Munch & Barr, 2001) Slow-release is also useful for coastal agriculture (Bashan & Bashan, 2004). Struvite provides nitrogen and phosphorus, but also magnesium which is vital for chlorophyll in plant leafs. Struvite is effective at acidic soil types and moderately alkaline. Struvite is effective fertilizer because 1 kg of struvite per day can fertilize 2.6 ha when applied at the rate of 40 kg d^{-1} y^{-1} (EFMA, 2000 & Zheng et al. 2004) Struvite doesn't burn the plants, even when high application rates, because it contains little of ammonium. (Munch & Barr, 2001) Struvite is most useful for phosphorus addition for area with phosphorus deficiency as struvite contains ratio of 1:1 of phosphorus and nitrogen. Struvite precipitation fertilizer has also advantage compared to raw manure fertilization. Manure fertilization could lead to easily overuse of phosphorus when nitrogen needs are satisfied with manure fertilization. Excess phosphorus of manure could be handled lowering manure phosphorus content by struvite precipitation. Struvite is easy to dry, handle, market and transported to location at the fraction of the cost when compared manure or compost. Phosphorus recovery as struvite from livestock waste and reuse can

decrease phosphorus load from livestock farming and produce valuable resource and income for farmers. (Massey et al. 2009) Struvite could be also produced effectively by chemical processes from its raw materials of phosphoric acid, ammonia and magnesium oxide, but material costs are usually prohibitive. MAP has been used commercially for tree seedlings, turf vegetables and flowers. (Doyle et al. 2003)

Commercially struvite has been produces only for couple of places. Japan has struvite fertilizer plant which produced struvite from anaerobic digestate and is sold for fertilizer company where it is mixed with other fertilizers. These fertilizers were used for paddy rice, vegetables and flowers. Produced struvite fertilizer contains low concentrations of heavy metals and organic pollutants. Plant uses fluidised bed reactor to crystallize struvite (Figure 7). (Ueno & Fujii, 2001).

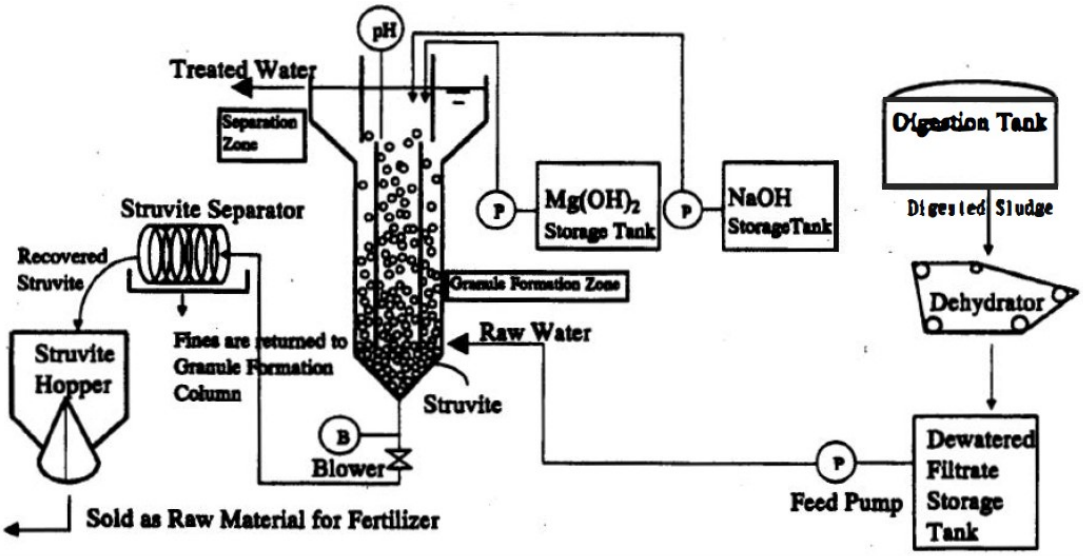


Figure 7. *Schematic picture of the struvite fertilizer plant in Japan (Ueno & Fujii,2001)*

Ostara Nutrient Recovery Technologies based in Canada provides struvite crystallization reactors for use of industry and waste water treatment plants to recover nutrients from their waste water effluents. Company has delivered nutrient recovery systems (Figure 8) in various locations North America and Europe. These systems can produce pelletized fertilizers for agricultural use. (Ostara Nutrient Recovery Technologies, 2017)

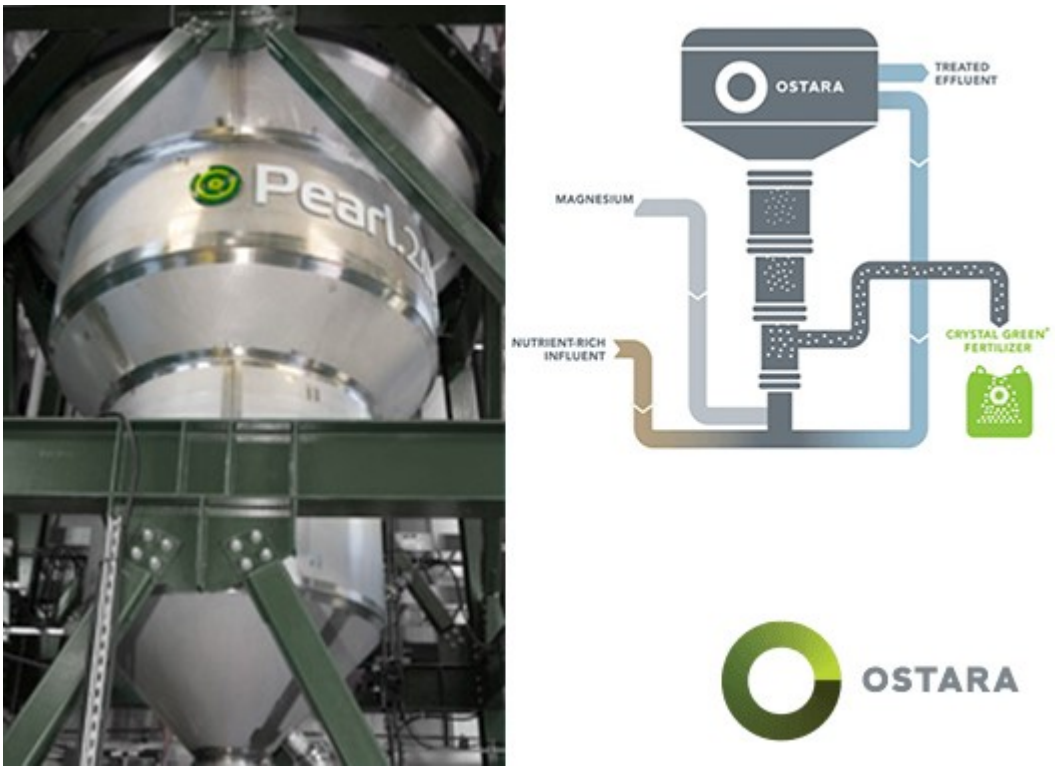


Figure 8. *Ostara nutrient recovery reactor for producing struvite fertilizers. (Ostara Nutrient Recovery Technologies, 2017)*

Most of the anaerobic digestate types contain varying amounts of heavy metals and therefore can affect quality of struvite and fertilizer possibilities. Digestates and waste usually contain toxic elements and varying metals, such as lead and mercury. Heavy metals can be captured in struvite crystals in nucleation process and crystal growth process. Although struvite might contain heavy metals it is usually in legal limits. (Taddeo et al. 2018)

3.8 Effects of temperature to struvite

Struvite solubility is depended on solution temperature. Increasing temperature is shown to increase solubility in temperature range of 10-65°C and maximum solubility to be in temperature 50°C. Temperatures above 64°C have been found to change struvite crystal structure and affect on struvite solubility. (Doyle & Parsons, 2002) Figure 9 represents the solubility curve of struvite.

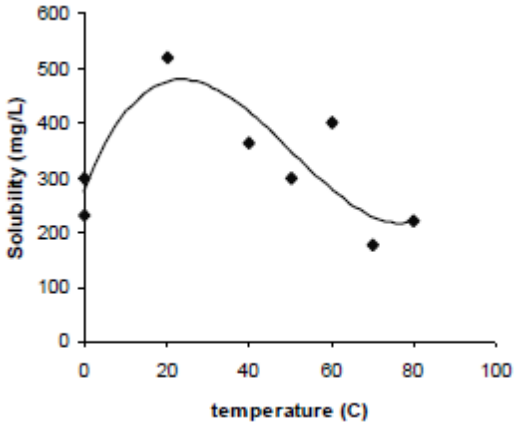


Figure 9. *Solubility curve of struvite in different temperatures.(Borgerding 1972)*

Struvite is found to decompose in higher temperatures. Struvite have gradual decrease of ammonia and has been observed to transformed to bobierrite when boiled (<100°C) for 24 h. Boiling struvite will cause it to lose five water molecules from it's structure and transformed to dittmarite, the monohydrate of struvite. (Bhuiyan et al. 2008) Transfer routes of struvite temperature treatment are shown in Figure 10.

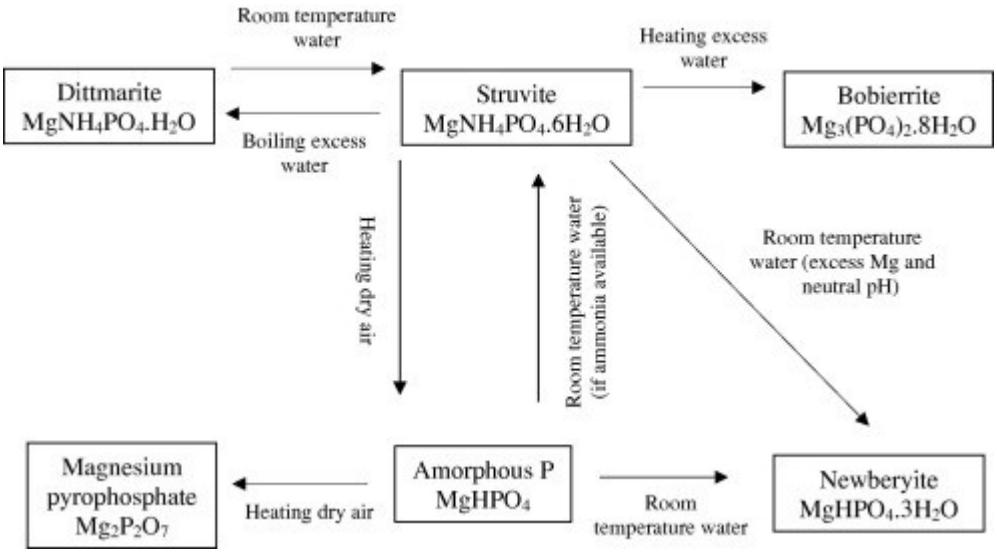


Figure 10. *Transformation mechanisms of various struvite phases (Bhuiyan et al. 2008)*

Struvite transformation to dittmarite could be used for phosphorus recovery from wastewaters, but economics of the process haven't been proven. Dittmarite decomposition temperature was found to be around 220°C and transform to amorphous magnesium phosphate ($MgHPO_4$) losing its ammonium. (Bhuiyan et al. 2008)

3.9 Economics of struvite production

Phosphorus recovery from waste as struvite has many advantages. Struvite helps reduce waste phosphorus concentration, so it can be used without excess phosphorus on agriculture and produced fertilizer can be sold and create income. However, adapting struvite crystallization process depends on economical sustainability. Cost effective production has to account i.e. chemicals, operating, maintenance and energy costs. (Le Corre et al. 2009) Cost of struvite is mainly depended on used chemical amounts and costs of these chemical for precipitation. Most studies have used high amounts of magnesium substrates and NaOH to adjust pH level. NaOH could be responsible 97% of the chemical expenses. (Jaffer et al. 2002) One possibility is use air stripping to reduce soluble CO_2 to increase pH and reduce NaOH use (Battistoni, 2004). Using $Mg(OH)_2$ substrate can reduce also costs because it's cheaper than $MgCl_2$ and it can also increase pH level (Von Munch & Barr, 2001). Using seawater as magnesium source is reported to have same phosphorus removal rates as $MgCl_2$ and could be solution for production sites in coastal areas. Limiting energy consumption for pumping and mixing can reduce the costs, and it can be achieved with auto-nucleation of struvite as seeded crystallization using seed particles i.e. sand. (Battistoni et al. 2005)

Market value of the struvite fertilizer and value of phosphates is considerable factor for economics. The profitability of struvite fertilizers depend on the profits generated by sale. Full scale applications are still very limited so estimating economical value is difficult to assess as it depends on rates of production and demand for struvite fertilizer. (Gaterell at al. 2000) Market price of the phosphate rock still decides how feasible option struvite fertilizers are and these prices have been relatively low for recent years. However, struvite precipitation could improve handling costs of sludge disposal and reduce sludge volumes and therefore be economical option. Struvite precipitation as a prevention of scaling could generate significant savings for WWTP's and biogas producers (Le Corre et al. 2009)

3.10 Struvite precipitation from swine wastewater

Struvite precipitation have been researched with swine wastewater (Liu et al. 2011 & Romero-Guiza et al. 2015), anaerobically digested swine sludge (Song et al. 2011) and using synthetic swine wastewater (Song et al. 2007). Swine wastewater contains high concentrations of phosphorus and nitrogen. Romero-Guiza et al. (2015) measured 2110 mg L^{-1} of N-NH_4^+, and 53 mg L^{-1} of P-PO_4^{3-} from swine wastewater, and also cations 45 mg L^{-1} of Mg^{2+} and 163 mg L^{-1} of Ca^{2+}. Swine wastewaters have usually more nitrogen than phosphorus and sometimes phosphorus is added for nitrogen removal (Liu et al. 2011). Anaerobically digested swine manure has usually similar characteristics as undigested swine manure (Liu et al. 2011). Different magnesium substrates and molar ratios have been studied for swine wastewater precipitation (Romero-Guiza et al. 2015).

Song et al (2007) studied phosphorus removal efficiency on synthetic swine wastewater with molar ratio of 1:1 Mg/P in pH levels from 8 to 12. Study concluded that most efficient pH levels were between 9.0 and 11.0 and decreased significantly above pH level 11.0 (Figure 11).

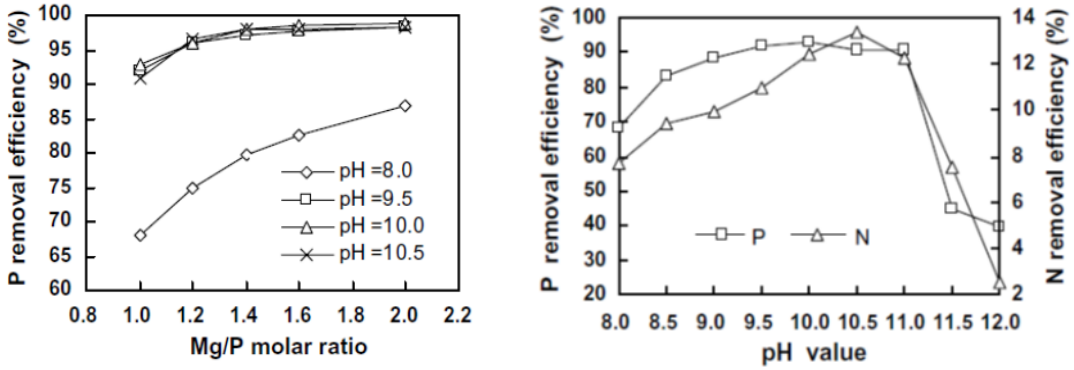


Figure 11. *Effect of molar ratio of Mg/P to phosphorus removal efficiency in different pH levels (left figure) and effect of pH to phosphorus- and nitrogen removal efficiencies (right figure) in synthetic swine wastewater. (Song et al. 2007)*

Song et al. (2007) showed that increasing molar ratio magnesium to phosphorus increases efficiency of phosphorus removal in synthetic swine wastewater (Figure 11). Research confirmed increased phosphorus removal efficiency with increasing magnesium concentration in all measured pH values. Most significant increase was measured in pH 8.

4. MATERIALS AND METHODS

4.1 Anaerobic digestion of swine manure sludge

Reactor for AD was continuously stirred reactor. Volume of the reactor was 4000 ml. HRT was set to 20 days which is typical for biogas reactors. Added substrate and extracted effluent volume would be then 280 ml when reactor feeding is done 5 times per week. Temperature was set to mesophilic range 36-37°C by circulating heated water in heating pipes around the reactor. Mixing was done by agitator which was set to around 30 RPM. Reactor was inoculated by anaerobic digester sludge from biogas reactor of Huittinen. Swine manure sludge fed to the reactor was from swine farm in Pirkanmaa.

Measurements of digester reactor performance were started 14 days after reactor inoculation. Effluent pH, COD, VFA and soluble cations were measured during operation. Gas volume and its composition were measured from gas samples. Ammonia and dissolved orthophosphate were measured from the effluent.

4.2 Struvite precipitation experiments

Struvite precipitation experiments were done using digestate effluent from the reactor setup and raw swine manure sludge. Digestate were collected middle of the digestion run about 3 week's effluent and mixed. Effluent was centrifuged in 4500 RPM and supernatant was extracted by decanting liquid phase so that most of the solids were separated from the liquid. Same treatment was done also for swine sludge. Acid treatment experiments were done using uncentrifuged digestion effluent. Soluble ammonium, phosphate and cations were measured from digestate mix and swine manure before experiments.

Struvite precipitation experiments consisted at six different parts (Table 4).

1. Optimal pH for precipitation was tested using pH range of 8-11.5. Centrifuged effluent was measured 100 ml in beaker glass. Magnesium substrate was chosen to be $MgCl_2$ in 1.5 M concentration. Magnesium substrate was added 100 µl to achieve over 2 times of molar ration to phosphate. Higher pH than 8 (natural pH level) was adjusted using 10 M NaOH solution and used amounts were written down. Solution was mixed using magnetic stirrer at 200 RPM for reagent adding and lowered to mixing of 60 RPM for 5 min. After mixing solution was let to settle in room temperature for 60 min. Solution were stored in fridge for later analysis. Two batches were made for all pH levels with 0.5 differences. Phosphate and ammonium were measured after 7 days of precipitation.
2. Difference measurements between magnesium substrates were done with MgSO4 and without added magnesium substrate. Tests were done same way as pH test. Duplicates were made for each experiment, but only final pH of 10 was decided to be tested, because it is the usual optimal pH range of precipitation (pH 9-10). Phosphate and ammonium were tested as in optimal pH test.
3. Precipitation time effect on precipitation efficiency was tested using batch from pH tests at pH level 11.5 for analysis of end of the pH range. Samples for phosphate analysis were taken from start of the precipitation to 10 days after precipitation.
4. Precipitation experiment with swine manure was done using raw swine manure sludge which was centrifuged and supernatant was separated as in other experiments. Substrate of $MgCl_2$ 1.5 M was added 200 µl to 100 ml of supernatant to achieve over 2 times of molar ratio to phosphate. Natural pH 7 and optimal precipitation pH 10 was tested. After precipitation, phosphate and ammonium analysis were done same as in section 1.
5. Measuring available orthophosphate released by acid treatment, digested effluent was measured 130 ml in beaker glass and 5 ml sample was taken starting at original pH level 8 and continued to pH level of 3, so 6 samples was taken at levels 8,7,6,5,4 and 3. Lowering pH was done using H_2SO_4 solution concentrations of 1 M and 10M. Phosphate concentrations were measured from the samples immediately.
6. Testing acid treatment-precipitation was done using 150 ml of digestate mix and pH was lowered to 3 using 10M H_2SO_4 solution while mixed by magnetic stirrer 60RPM. Acid treated mixture was then centrifuged and decanted. Released phosphorus was measured from solution Precipitation was done by adding 1.2 ml of 1.5 M $MgCl_2$ to 100 ml of treated supernatant. Solution pH was raised using 10 M NaOH solution while mixing with magnetic stirrer at 200 RPM. Phosphorus and ammonium analysis were done after 7 from precipitation.

Table 4. *Struvite experiments done with description of materials used and pH*

Experiment	Precipitation material	Magnesium substrate	pH adjustment	Starting pH	Final pH
Optimal precipitation pH	Digestate	$MgCl_2$	NaOH	8	8 to 11.5
Precipitation without magnesium substrate	Digestate	No added magnesium	NaOH	8	10
Precipitation with magnesium sulfate substrate	Digestate	MgSO4	NaOH	8	10
Precipitation time effect on phosphorus removal efficiency	Digestate	$MgCl_2$	NaOH	8	11.5
Precipitation on untreated swine manure sludge	Swine sludge	$MgCl_2$	NaOH	7	7 & 10
Acid digestion treatment on releasing phosphorus	Digestate	No added magnesium	H_2SO_4	8	3
Acid digestion treatment phosphorus removal efficiency	Digestate	$MgCl_2$	NaOH H_2SO_4	8 (treated 3)	10

4.3 Analytical methods and calculations

Ammonia concentrations were measured with ammonia measurement kit LCK303 (Hach, USA). Dissolved orthophosphate was measured phosphorus measurement kit LCK348 (Hach, USA). Samples were filtered with 0.45 µm syringe filters before analysis.

COD samples were stored adding H_2SO_4 to final concentration of 10 mM. COD was measured by standard Finnish standard SFS 5504 (1998). Samples were filtered with 0.45 µm syringe filters.

VFA samples were filtered with 0.45 µm syringe filters and stored in the fridge. VFA analyses were done using Shimadzu GC2010 gas chromatograph. Column temperature 50°C, detector temperature 250°C, helium carrier gas and column flow of 20 ml/min.

Collected gas volume was measured using water-displacement method. Collected and measured gas was divided by days to last measurement to get daily average gas production. Gas composition was measured using Shimadzu GC2010 gas chromatograph. Column temperature 80°C, detector temperature 110°C, carrier gas was nitrogen gas, and column flow 20 ml/min.

Cation samples were filtered with 0.45 µm syringe filters and stored in fridge adding HNO3 to 10 mM concentration. Available cations were measured using ion chromatograph Dionex DC120 (Dionex, USA) using eluent 20mM methanesulfonic acid at 1 ml/min flow rate with helium carrier gas. Standards were made by SFS-EN ISO 14911.

Microscope pictures were taken by field emission scanning electron microscope (FESEM, ULTRAplus, Zeiss, Germany) with energy dispersive spectrometer (EDS, XMaxN, Oxford Instruments, UK) and sample was fixed on the aluminium SEM stub by carbon tape followed by carbon coating to avoid sample charging during SEM studies.

The XRD measurements were carried out with a Panalytical Empyrean X-ray diffractometer and monocrhomatized CuKα radiation (λ= 1.5418 Å) over a range of $10° < 2\theta < 80°$. The data were analysed with HighScore plus software. The program employs The International Centre for diffraction Data (ICDD) for phase analysis.

Total solids were measured using gravimetric analysis. Liquid samples were treated in 105°C for 24 h.

5. RESULTS AND ANALYSIS

5.1 Anaerobic digestion of swine manure sludge

Anaerobic digester reactor effluent pH was measured (Figure 12) to ensure working AD process, from starting of the measurements (day 1) to the shutdown of the reactor (day 50).

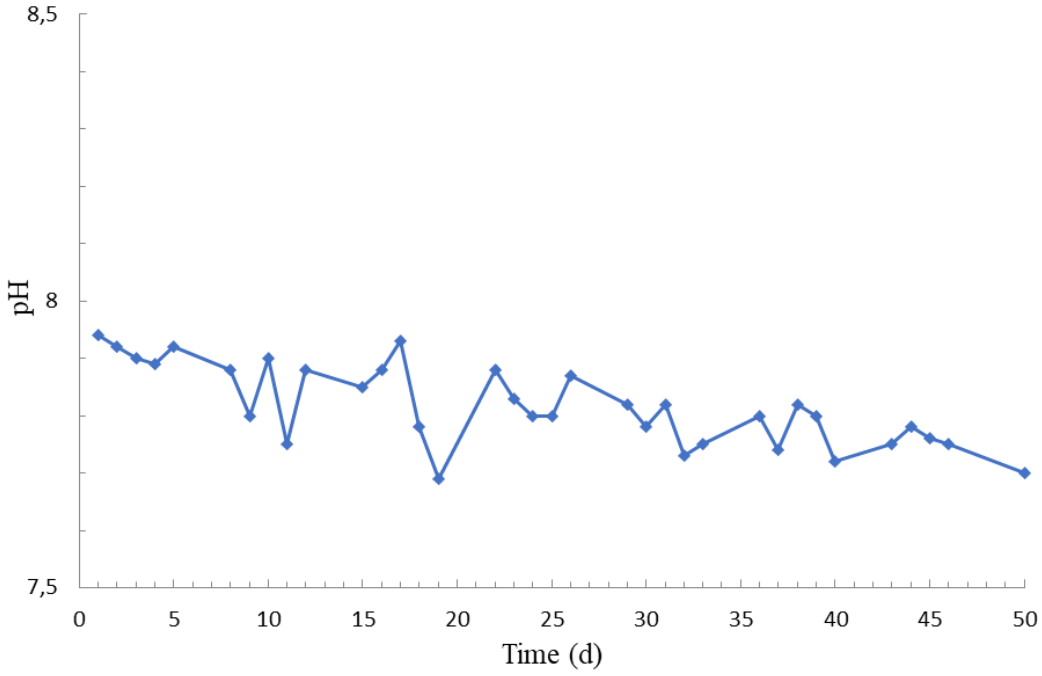


Figure 12. *Anaerobic digester effluent pH.*

Starting pH was 7.94 and in the end pH (day 50) was 7.70. Effluent pH lowered gradually but stayed over neutral. Possible reasons for lowering pH could be stabilizing conditions inside the reactor or lowering substrate pH level. Faster processing speed of the reactor could reason for the lower pH. Digestate pH level stayed within the optimal pH range for anaerobic digestion of 7.0 and 8.0 (Kiran et al. 2016). Decrease of pH level might be from increasing metabolites such as acetate. However, digester seems to handle well the with the decreasing pH level.

Volumetric ration of carbon dioxide and methane was measured during digestion (Figure 13). Methane level of the biogas was most of the time over 60% and under 80%.

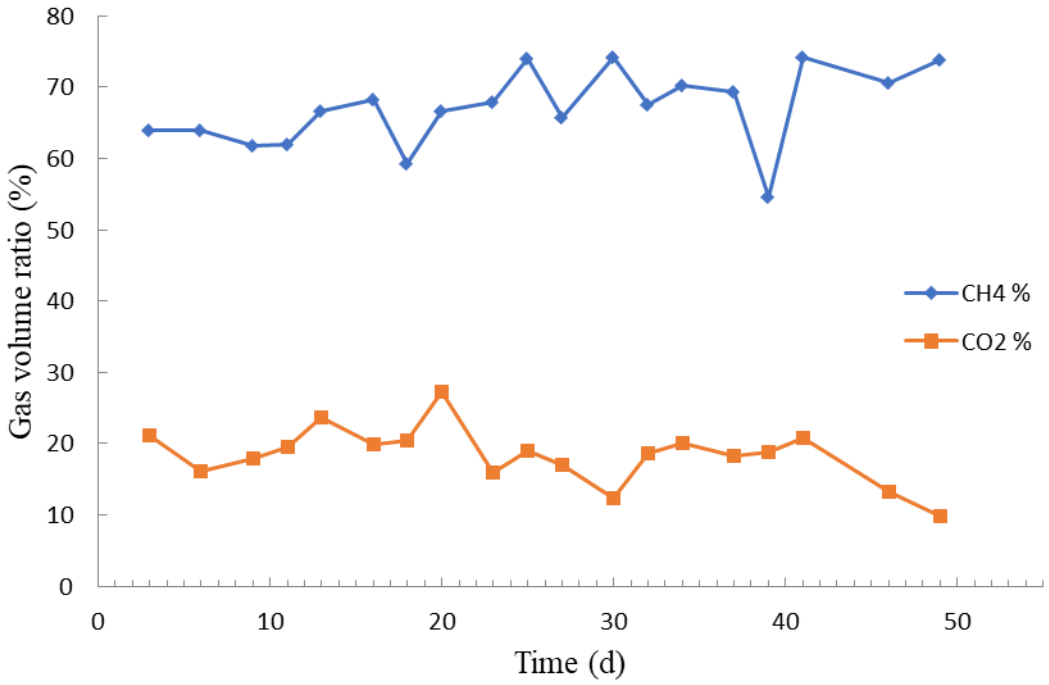


Figure 13. *Digester CH_4 and CO_2 gas volume ratio in %.*

Gas components maximum, minimum and average ratios are presented in Table 5. Average methane content of the gas was 67% and carbon dioxide 18%

Table 5. *Digester gas components maximum, minimum and average ration in %.*

Gas	Max (%)	Min (%)	Average (%)
CH_4	74,22	54,51	67,08
CO_2	27,27	9,90	18,42

Amount of gas was measured during reactor run by displacement method. Gas production varied from day 1 to 30, but stabilized later between 1-1.5 L/d.

Chemical oxygen demand of the digestate varied between 3.2-5.0 g/L (Figure 14). Only acetate was detected from VFA components.

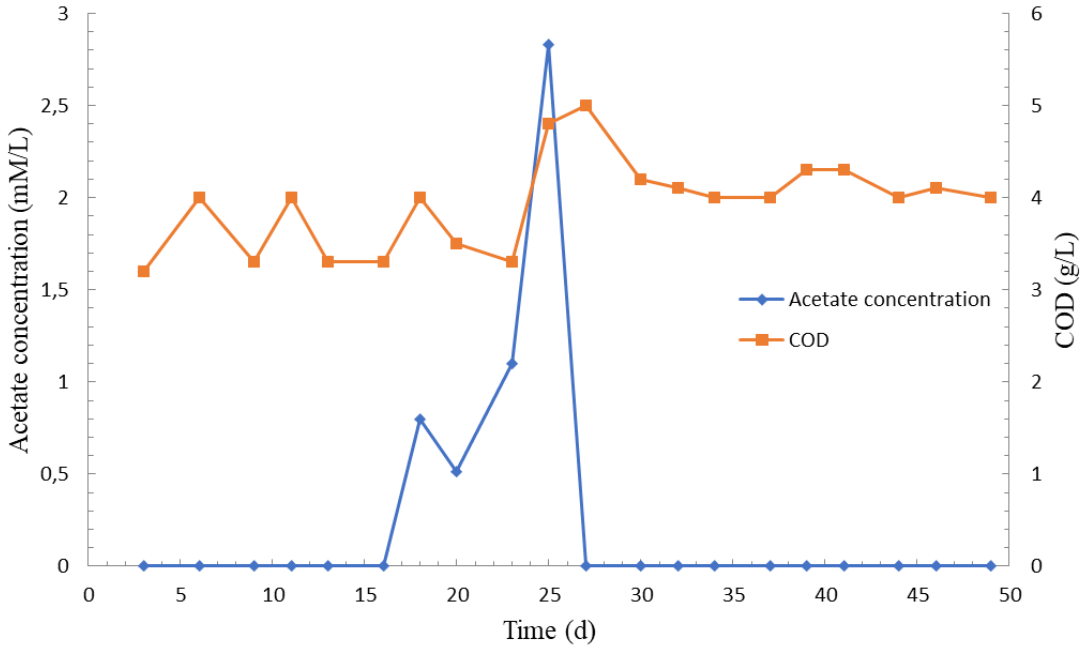


Figure 14. *Soluble chemical oxygen demand (top line) and VFA concentration (under line) of the digestate.*

Day 25 had increased level of COD (4.8 g/L) compared to day 23 (3.3 g/L). Increased concentration might have been caused by change in influent substrate or other environmental change. Average soluble COD from digestate was 3.9 g/L and swine manure COD 4.4 mg/L. Temperature changes could have change volatile acid-forming bacteria balance and accumulation of acetate. Temperature changes can also effect on methane forming bacteria activity and accumulation of VFA. Acceptable VFA concentration is 50-200 mg/L (Gerardi, 2003) and maximum acetate concentration was 167 mg/L. VFA had also correlation with increasing COD level. From day 30 COD levels and acetate concentration seems to stabilize. Other VFA components couldn't be detected which can indicate good operation of the digester without accumulation of any VFA components.

Measured potassium, sodium, calcium and magnesium concentration in the digested effluent is presented in Figure 15.

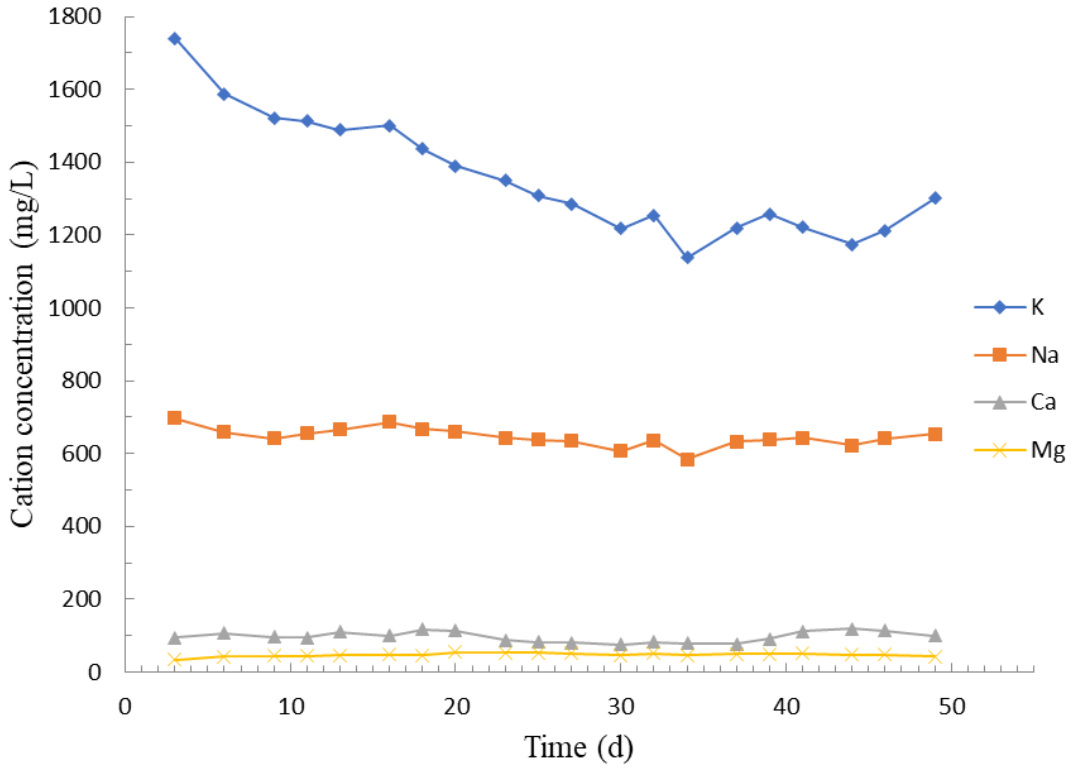


Figure 15. *Cation concentrations in the effluent as mg/L. Lines from top to bottom: Potassium, Sodium, Calcium and Magnesium.*

Most of the cation concentrations kept relatively stable, therefore maximum and minimum concentrations were close the average concentration (Table 6). Potassium concentration was detected to decrease over time, but could be explained by effect of inoculum. One possible explanation is potassium ability to crystallize to K-struvite, which was detected in XRD-analysis. Potassium concentration of the digestate is considered to be relatively high when compared to other digested materials.

Table 6. *Cation maximum, minimum and average concentrations of digested effluent.*

C (mg/L)	Na	K	Ca	Mg
Max	697	1740	120	55
Min	585	1137	75	35
Average	646	1356	97	47

Magnesium concentration was well below inhibiting concentration (1000 mg/L) and so was also sodium (35000 mg/L) level (Gearadi, 2003).

Ammonium and phosphorus were measured from the effluent. Measured ammonium levels as elemental nitrogen and phosphorus levels as elemental phosphorus are shown in Figure 16.

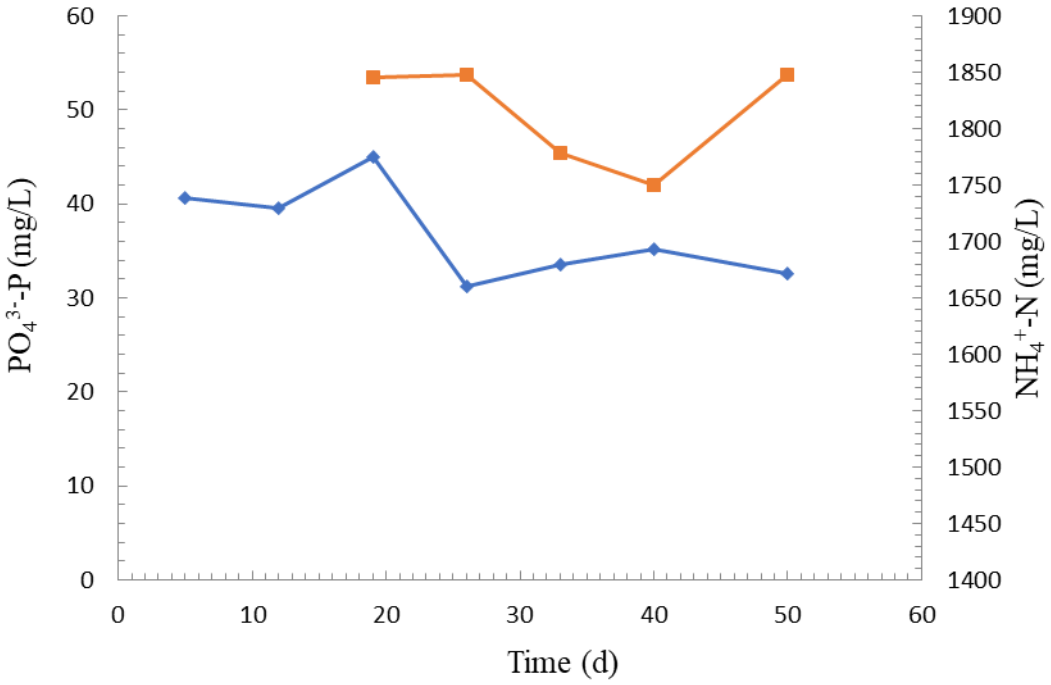


Figure 16. *Ammonium levels of the digestate as elemental nitrogen (upper line) and phosphate levels of the digestate as elemental phosphorus (lower line).*

Digester ammonical-nitrogen levels were below 1900 mg/L. Ammonium ions (NH_4^+) are used as nutrient by bacteria, but free ammonia (NH_3) is toxic for methane forming bacteria. Certain toxic ammonia levels haven't determined but ammonical-nitrogen levels over >3000 mg/L are toxic and lower levels when pH is high. (Gerardi, 2003).

Phosphorus concentration was slightly decreasing over time in the effluent and might be caused by precipitation as phosphates spontaneously in the reactor. Liquid composition has enough components (Ca^{2+}, Mg^{2+}, K^+, and NH_4^+) to crystallize all of the soluble phosphorus to phosphates.

Characteristics of the feedstock swine manure sludge and digestate are shown in Table 7. Also digested sludge mix for precipitation experiments is presented.

Table 7. *Characteristics of the used materials in digestion process and struvite precipitation experiments.*

Characteristic	Unit	Swine manure sludge	Digestate swine manure sludge (average from measurements)	Digested swine manure sludge mix for precipitation experiment
PO_4^{3-}-P	mg/L	42	37	26
NH_4^{+}-N	mg/L	1923	1847	1830
COD	g/L	4.4	3.9	NM
pH		7.0	7.8	8.0
TS	%	7.2	4.6	3.6
Mg	mg/L	58	47	NM
Ca	mg/L	252	97	NM
K	mg/L	1107	1356	NM
Na	mg/L	634	646	NM

Higher pH in experiment digestion sludge compared to digestion sludge may have caused by air stripping of carbon dioxide when storing the solution in the fridge (Battistoni et al. 1997), because pH of the digestion effluent was measured right after feeding the reactor when CO_2 was soluble in the liquid. Also soluble phosphate concentration was noticed to decrease, possibly from spontaneous precipitation in the liquid.

5.2 Struvite precipitation experiments

5.2.1 Optimal precipitation pH

Removal efficiency was tested from original pH 8 of the digestate to 11.5 on every 0.5 difference of pH. Optimal precipitation pHs with standard deviations are presented in Figure 17. Phosphorus removal efficiency increased from pH level 8 to 10.5 and started to decrease at pH 11 level. Removal efficiency decreased significantly from 91% at pH 11.0 to 83% at pH11.5. Highest standard deviation rate was calculated between two batches at pH level 8 and 11.5 level.

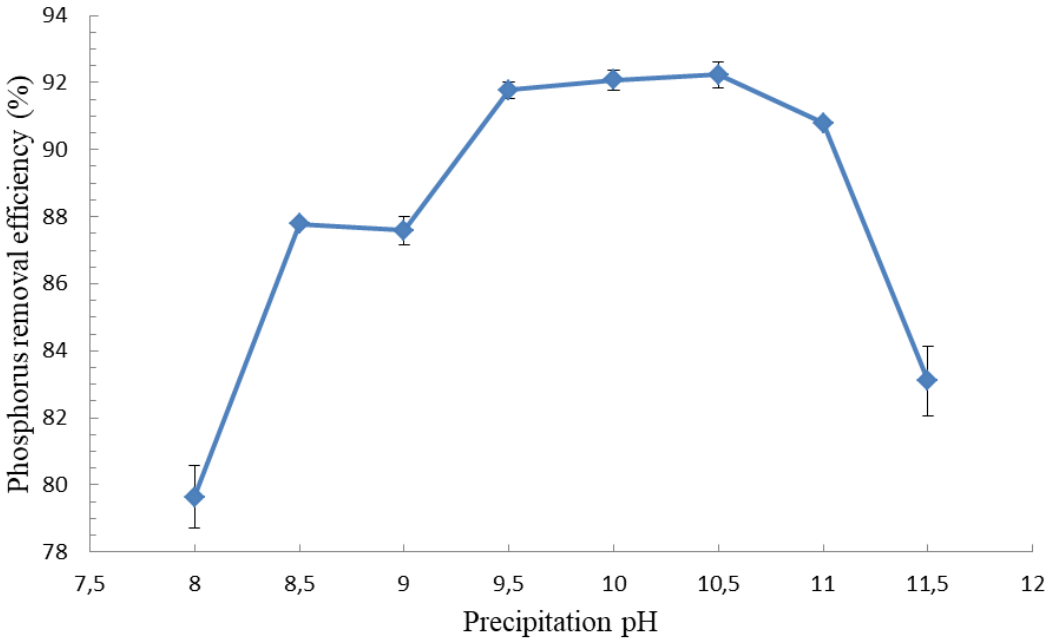


Figure 17. *Phosphorus removal efficiency in different precipitation pH. Error bars are standard deviations between measurements of two batches.*

Soluble calcium in the digestate might react with phosphate and help with precipitation of phosphate, especially in higher pH (Hao et al. 2008) Calcium apatite precipitation could also explain higher removal efficiency at pH 9.5 and higher because it's solubility decreases at these pH levels. Decreasing solubility of struvite in higher pH (Doyle & Parsons, 2002) suggest that removal efficiency is higher in increased pH, because more struvite is precipitated. Song et al. (2007) got also lower phosphorus removal on pH levels of 8 which increased to pH 11.0 level. Likewise, they also measured high decrease on removal efficiency at pH 11.5 level. Taddeo et al. (2018) also showed that the amount of produced struvite is inversely proportional to the alkalinity of the precipitation solution.

5.2.2 Buffer capacity of precipitation effluent

Needed hydroxide ion amount to raise alkalinity of the precipitation solution in optimal pH experiment is shown in Figure 18. Added molar amounts are from optimal precipitation pH experiment, where 10 M NaOH solution was added to increase digestate pH level, which is used often in struvite experiments.

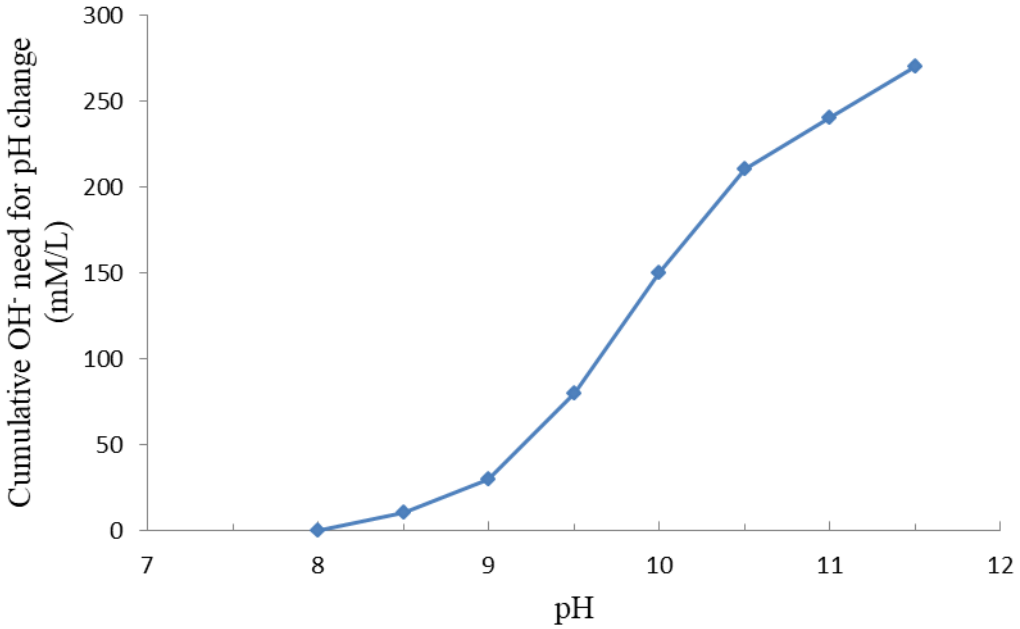


Figure 18. *Cumulative used OH^- for raise the precipitation solution in optimum pH experiment*

Added hydroxide raises exponentially from pH 8 to pH 10. Needed hydroxide amount to raise pH starts to decrease from above pH level 10 and might be caused by decreased precipitation of calcium and magnesium hydroxides.

5.2.3 Precipitation efficiency on different magnesium substrates

Magnesium substrate effect on removal efficiency of phosphorus were tested using no added magnesium and with $MgSO_4$ in pH level of 10. Phosphorus removal efficiency of magnesium sulfate and without added magnesium is shown in Figure 19. Measurements indicated that magnesium substrate type has no significant difference on phosphorus removal efficiency between magnesium sulfate (86% at pH10) and magnesium chloride (92% at pH10). Both of these magnesium substrates are highly soluble to water and therefore show no major difference in precipitation.

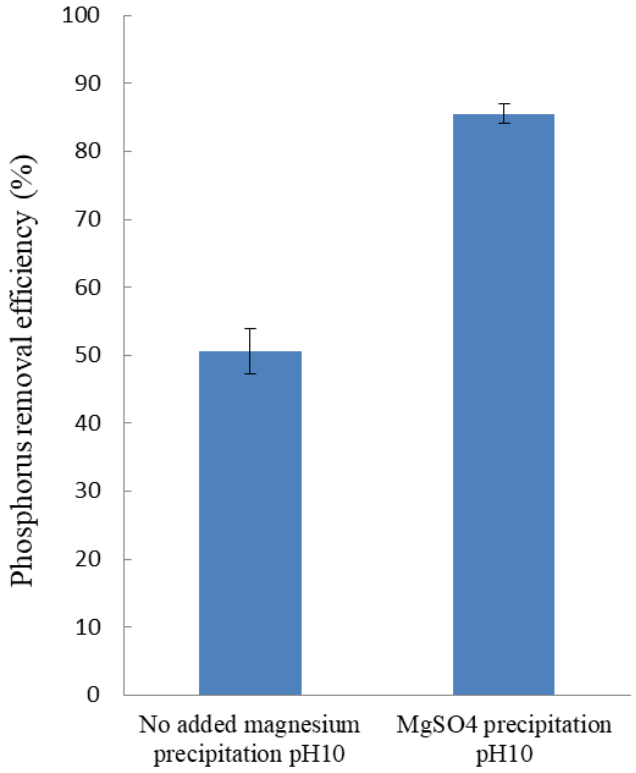


Figure 19. *Phosphorus removal efficiency without added magnesium substrate and with magnesium sulfate in precipitation pH10. Error bars are standard deviation of two batches.*

Precipitation without added magnesium however had significant effect on phosphorus removal efficiency. Only 51% of available phosphorus was removed from the liquid and it happened when ratio of magnesium and phosphorus was already over 2:1 by original concentration of magnesium. More magnesium ions in the solution could increase more interactions with phosphorus and start crystallization process more likely. Also significant amount of magnesium could precipitate as magnesium carbonate $MgCO_3$ and removed from available magnesium for struvite precipitation.

5.2.4 Effect of precipitation time on phosphorus removal efficiency

Precipitation experiment was done using pH 11.5 batch from pH-efficiency experiment and measuring phosphorus concentration from precipitation start to day 10. Precipitation time on phosphorus removal efficiency is shown in Figure 20.

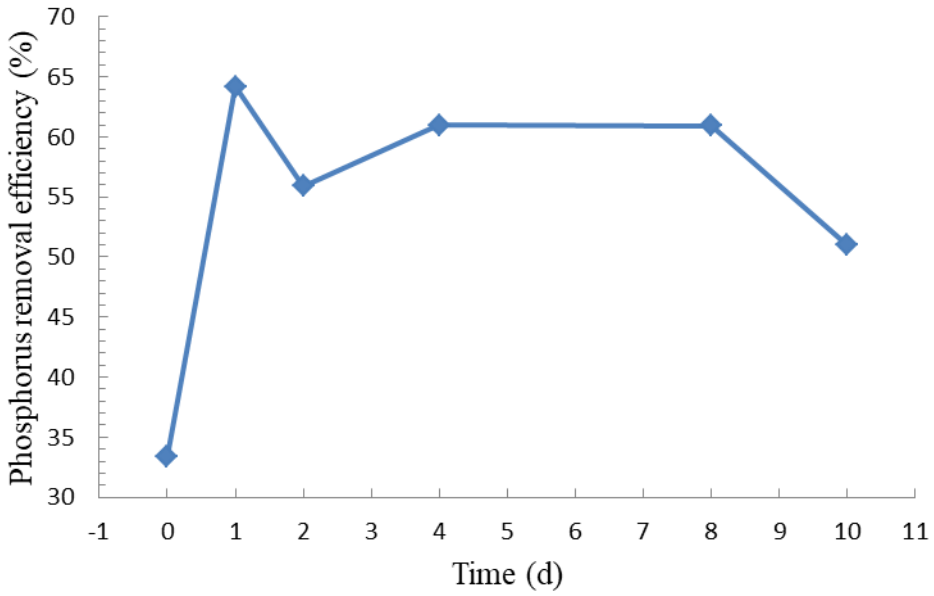


Figure 20. *Effect of precipitation time on phosphorus removal efficiency for batch pH 11.5 in 10 day period.*

Higher pH increases growth rate of the struvite crystals (Ohlinger et al. 1999, Le Corre et al. 2009) and therefore might resulted relatively rapid increase in precipitation efficiency between start and day 1. Removal efficiency seems to settle over 55% and indicate that equilibrium in dissolving has been reached. However measurements have large errors, because experiment was done only in one batch and from one pH level. Other pH batch could also have different results. Longer measuring period could have confirmed that precipitation reached equilibrium.

5.2.5 Swine manure sludge struvite precipitation

Struvite precipitation efficiency was tested using swine manure sludge as feedstock and precipitation pH 7 and 10 (Figure 21). Swine sludge had higher starting phosphorus concentration (42 mg/L) than digested sludge (26 mg/L)

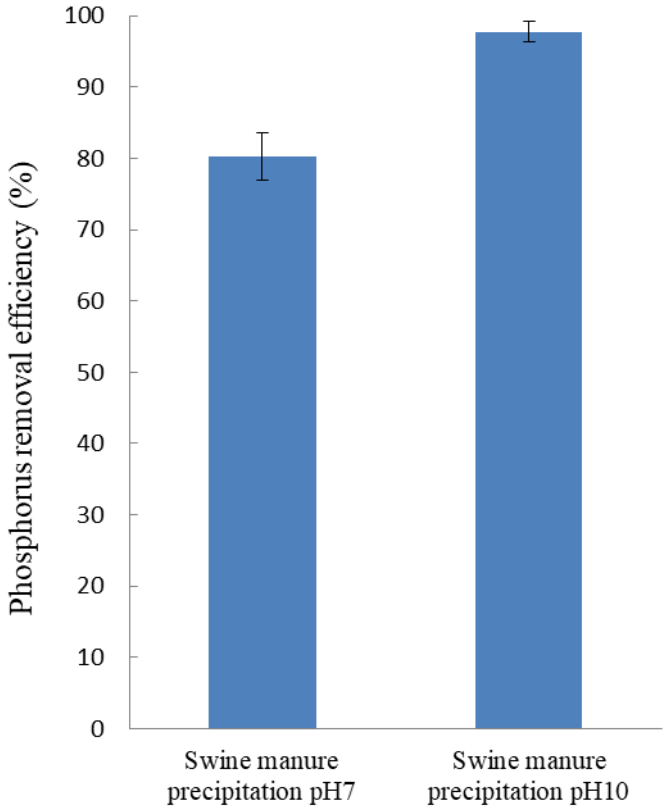


Figure 21. *Phosphorus removal efficiency for swine manure feedstock in pH 7 and 10. Error bars are standard deviation of two batches.*

Precipitation in original pH 7.0 achieved phosphorus removal efficiency of 80% and pH 10 approximately efficiency of 98% removal. Molar ratio of Mg/P was over 3:1 after magnesium addition. Liu et al. (2011) found in their studies that removal efficiency over 90% can be achieved using raw swine manure sludge and over 1:1 Mg/P molar ratio at original pH level. Original pH for their study was 8.35, which is higher than in this study (7.0).

5.2.6 Acid treatment and precipitation

Released phosphorus by acid treatment was tested by lowering digestate pH using H_2SO_4 solution and taking samples from each pH level for phosphorus and cation analysis. Acid treatment experiments results for phosphorus release are shown in Figure 22. Results are calculated by subtracting natural phosphorus level of digestion effluent (26 mg/L) from measured level.

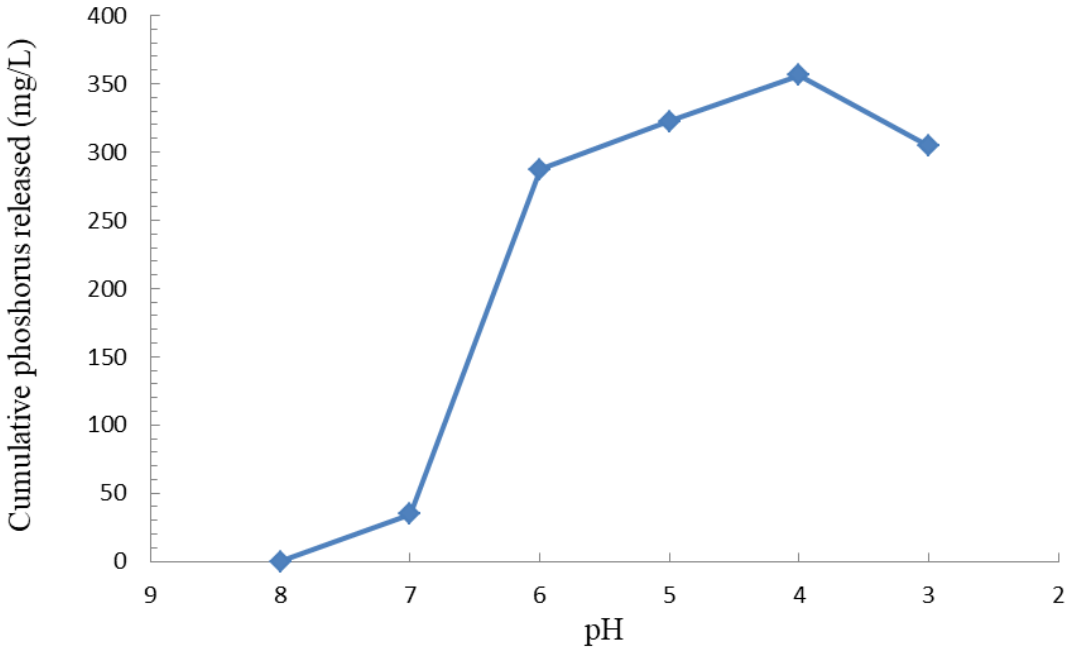


Figure 22. *Cumulative released phosphorus from pH 8 to 3 per treated Litre of digestate*

Most of the phosphorus was released to soluble form when pH was decreased to level 6. Decreasing pH level more increased released phosphorus in levels 5 and 4, but decreased in level 3. Decreasing phosphorus level at pH 3 was unexpected, but could be explained by possible measuring error. More experiment batches and measurement could have confirmed results. Maximum released phosphorus concentration was achieved at pH 4 for 356 mg/L and it means only 6.8% of the phosphorus was available from the beginning in soluble form. Schoumans et al. (2017) concluded that most of the available phosphorus in acid treated digestate will be released at pH 5 and there is no more phosphorus released at lower pH levels.

Needed H+ ion amount acid treatment phosphorus release experiment is shown in Figure 23. Digestate effluent was acid treated from original pH 8 to 3 level.

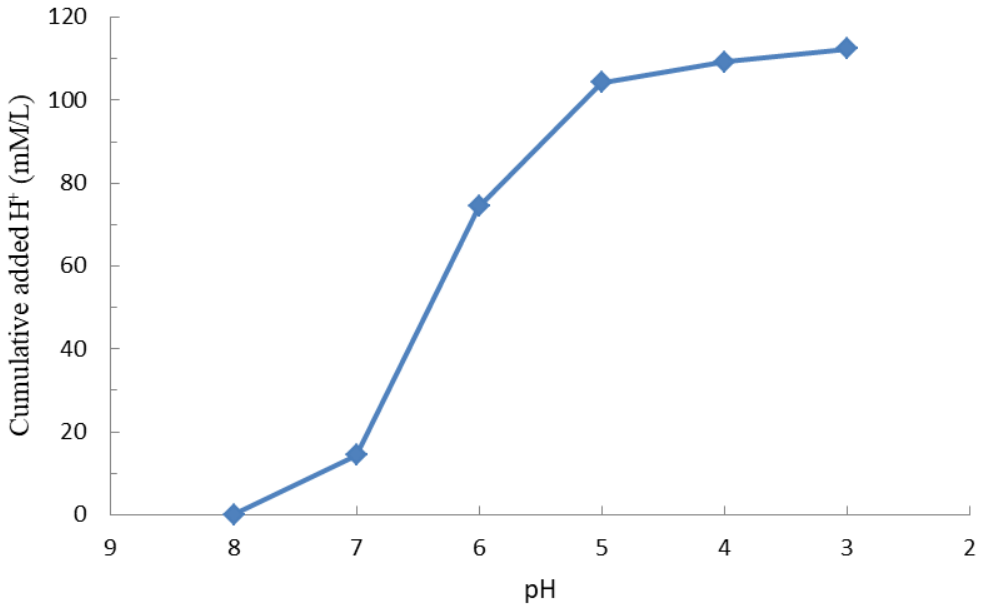


Figure 23. *Cumulative used H^+ to adjust the pH of digestate (H^+/L).*

Most of the added acid was consumed to decrease pH from 7 to 6. After pH 5 needed H^+ to lower pH decreased rapidly. During pH treatment experiment was observed that decreasing pH from 7 to 6 the solution started foaming heavily and was possibly caused by hydrolysis of organic matter and dissolution of precipitants, such as carbonates.

Released Mg^{2+} reached level of over 200 mg/L from starting concentration of 47 mg/L when pH was 5 or lower. Released Ca^{2+} reached concentration over 500 mg/L from starting concentration of 97 mg/L. Released magnesium and calcium are from precipitated magnesium- and calcium phosphates and other precipitants naturally occurring in the effluent. Some of these cations are released from their carbonates.

5.2.7 Cation concentration change after precipitation

Molar concentration change (%) of cations compared to phosphorus molar change from all of the experiments is presented in Table 8. Difference tells how much cation concentration change compared to phosphorus concentration (start 26 mg/L or 0.84 mM/L) meaning that -100% cation concentration change had similar molar concentration change as soluble phosphorus.

Table 8. *Molar concentration ratio change of soluble cations compared to precipitated phosphorus after precipitation.*

Precipitation experiment	Potassium Concentration change ratio (%)	Calcium concentration change ratio (%)	Magnesium Concentration change ratio (%)
pH8	-495	-248	-231
pH8,5	-382	-281	-181
pH9	-408	-284	-204
pH9,5	-315	-273	-193
pH10	-386	-265	-194
pH10,5	-350	-263	-171
pH11	-381	-269	-168
pH11,5	-364	-285	-378
No magnesium pH10	-539	-437	-361
MgSO4 pH10	-318	-286	-207
Swine manure pH7	-85	45	-65
Swine manure pH10	139	-305	-93
Acid treated	-20	-65	-105

Calcium concentration molar ration dropped similarly between precipitation pH range 8-11.5 and indicating that calcium precipitation was depended on phosphorus precipitation. Magnesium molar ratio was more than 2:1 compared to phosphorus amount at pH 8 and 11.5. Interestingly these two pH levels had the lowest removal rates of phosphorus. Potassium precipitation ratio seems to be fairly similar in all pH levels. Potassium change could tell that digested sludge precipitate more K-struvite. Swine manure precipitated less calcium at pH 7 than pH 10 and indicating that less calcium phosphate were precipitated. However it has to be noted, that rate of error could high because only one sample was taken for cation analysis from each batch.

5.2.8 Removal efficiency of ammonium

Removal efficiencies of free ammonium from the experiments are shown in Figure 24. Removal efficiencies are average of the measurements from duplicated batches.

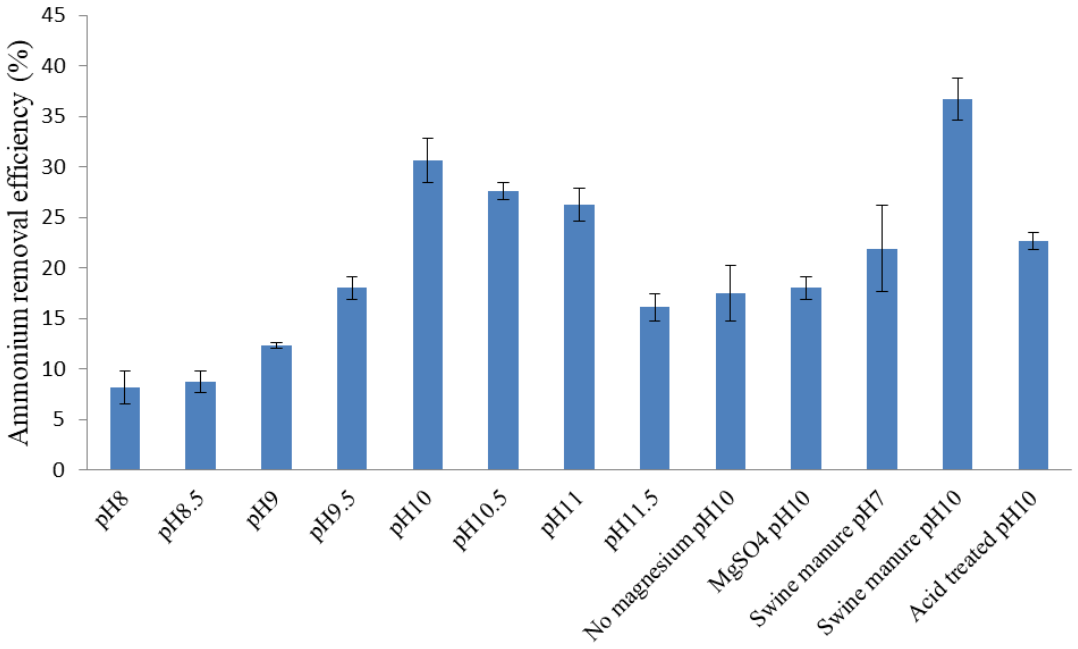


Figure 24. *Experiments removal efficiencies of ammonium. Error bars are standard deviations of the two batches.*

Ammonium removal efficiency increased with increased pH level. Ammonium removal efficiencies showed little correlation with phosphorus removal efficiency, and for example in optimal pH experiment pH 9.5 and pH 10 had similar phosphorus removal efficiencies but different ammonium removal efficiencies. Decrease might be caused by ammonium stripping where soluble ammonium (NH_4^+) was converted to ammonia gas (NH_3) and escaped from the liquid at higher pH levels. Also relatively long precipitation time (7 days) could have made possible to ammonium to evaporate as ammonia. Song et al. (2007) had maximum nitrogen removal efficiency of 13%, but precipitation time was set only for 2 h.

5.2.9 SEM analysis of precipitated crystals

SEM analysis was done to struvite crystals from acid treated batch (Figure 25). Other pictures from same crystal samples are in Appendix A. SEM pictures showed that crystal size is about 10 µm. Crystal sample was grinded, which might have affected on average crystal size and structure at least some of the crystals. However, SEM pictures showed several crystal to be plate shaped and with similar size. Acid treated batch had high starting phosphorus concentration, which could have impact on the relatively small crystal size.

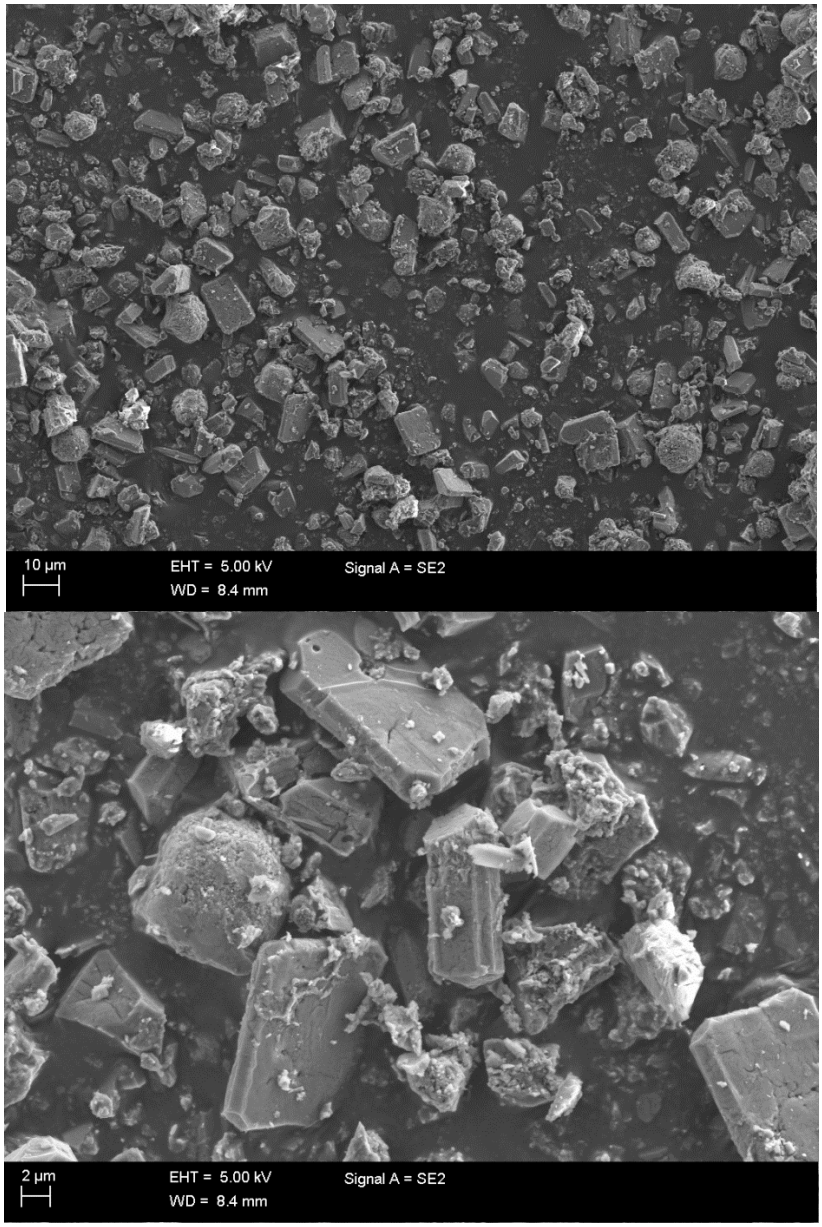


Figure 25. *SEM (magnified in below picture) from precipitated crystals in acid treated batch*

SEM elemental analysis pictures are shown in Figure 26. Other picture group of elemental analysis from same sample are in Appendix A

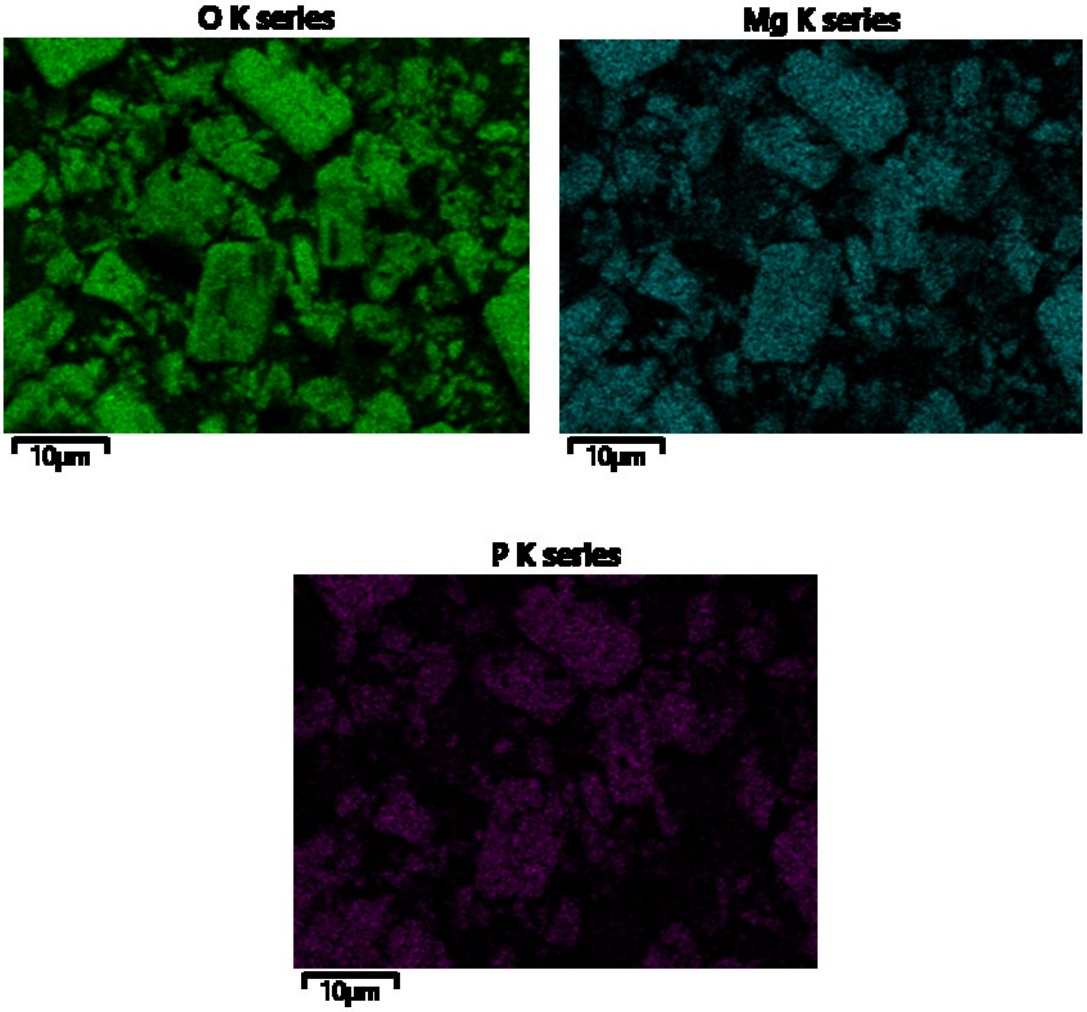


Figure 26. *SEM elemental analysis pictures of oxygen, magnesium and phosphorus*

Elemental analysis showed that plate shaped crystals contained oxygen, magnesium and phosphorus and indicating that crystals are likely magnesium phosphates or struvite containing these elements.

5.2.10 X-Ray diffraction analysis of precipitated crystals

All of the precipitated crystals from the experiments were analysed by XRD. Struvite crystals were XRD-analysed from dried crystal samples (Figure 27).

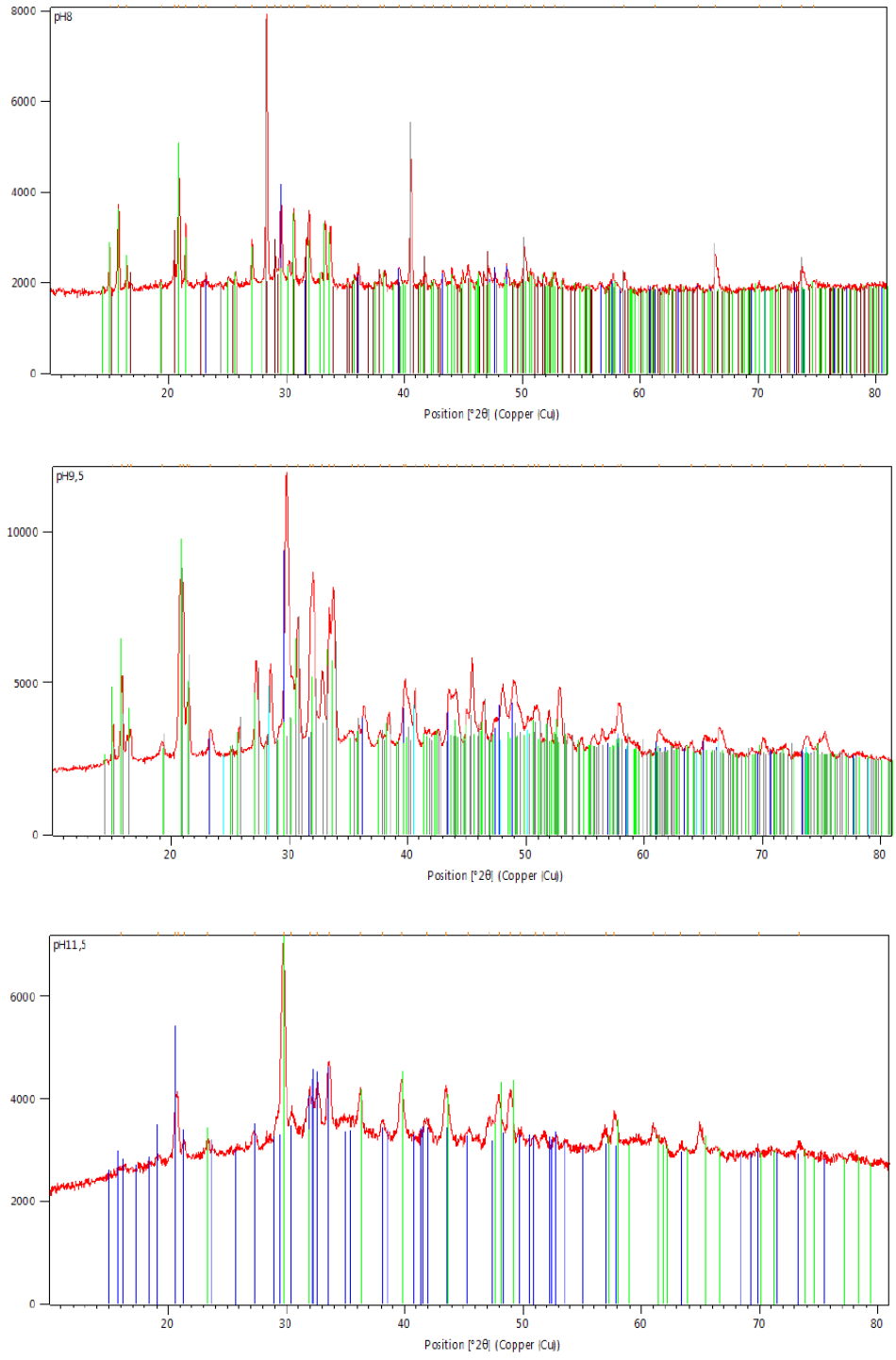


Figure 27. *X-ray diffraction pattern from pH 8 (top) pH 9.5 (middle) and pH 11.5 (low) batch crystals*

Diffraction patterns showed presence of MAP and K-struvite in all pH-experiment samples. Background noise was noticed to rise with rising pH level. Two different

carbonates ($MgCO_3$, $CaCO_3$) were detected in all batches. Also hazenite $KNaMg_2(PO_4)_2$ was detected in some samples. Precipitated salts KCl and NaCl was detected in some of the crystal samples.

Measured ratios of precipitate types are in Table 9. Molar ratio% are indicative and with rate of error. Also ratios are compared from detected crystal types and therefore inaccurate because all crystals aren't detected.

Table 9. *Measured molar ratios % of crystal from detected crystal types*

Precipitation experiment	Struvite (K-struvite & MAP)	CaCO3 $MgCO_3$ Calcite, Magnesia
pH8	55	30
pH8,5	44	50
pH9	60	35
pH9,5	86	12
pH10	76	24
pH10,5	37	21
pH11	20	29
pH11,5	31	28
No magnesium pH10	31	37
MgSO4 pH10	37	18
Swine manure pH7	72	18
Swine manure pH10	41	59
Acid treated pH10	35	29

Le Corre et al. (2005) showed that increasing molar ratio of calcium compared magnesium increases amorphous matter signal in XRD-analysis. Background noise was increased with calcium concentration. They confirmed to cause by amorphous calcium phosphates phases in the precipitation and be the reason why amorphous signal is increased when precipitation pH is increased. Calcium apatite tends to form at pH level of 9.5 and above (Doyle & Parsons, 2002) However, amount of amorphous material cannot be estimated reliably, because that would have been required amorphous standard measurements for XRD-analysis.

Most of the struvite was detected to be MAP in pH8 and 8.5. Struvite had double diffraction spike in pH 9 and 9.5 indicating that both K-struvite and MAP were present. After pH 10.5 only MAP was detected. However these results may have some error rate, because chemical structure of MAP and K-struvite is very similar (Taddeo et al. 2018).

Amount of calcium carbonate $CACO_3$ was detected to have increasing concentration between pH 8-9.5 and decreasing signal at higher pH indicating that concentration is decreased in higher than pH 9.5.

5.2.11 Struvite precipitation visual changes

Visual changes in precipitation solution are shown and compared in Figures 28 and 29. For the comparison there are original digestates. Solutions of pH experiment are shown in Figure 28 and other experiments solutions are shown in Figure 29.

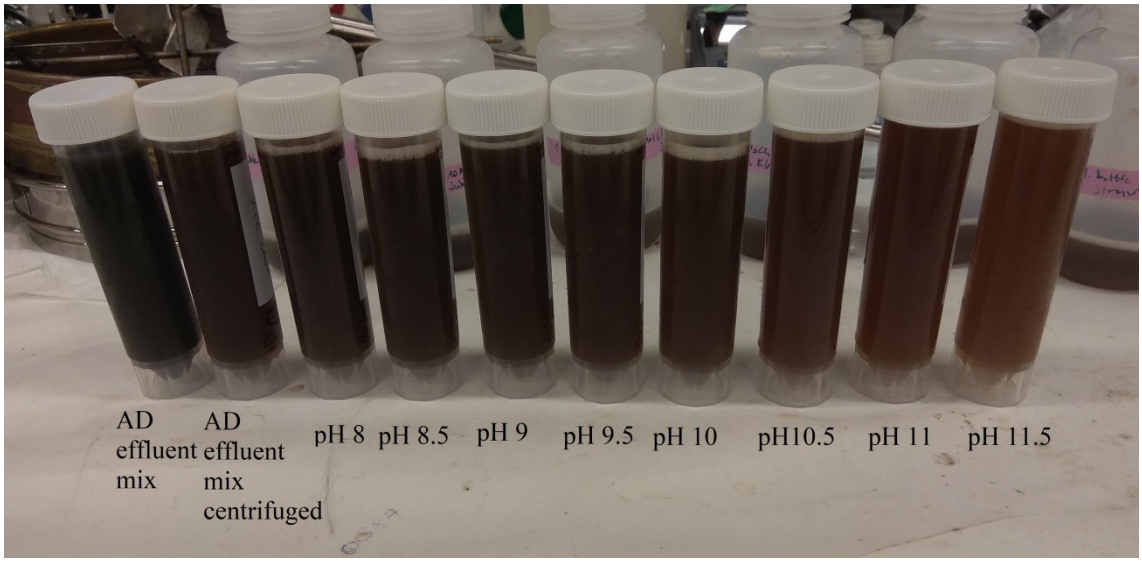


Figure 28. *Precipitation solutions of pH experiment after precipitation. From left to right: anaerobic digested effluent, centrifuged effluent and pH 8-11.5 solutions.*

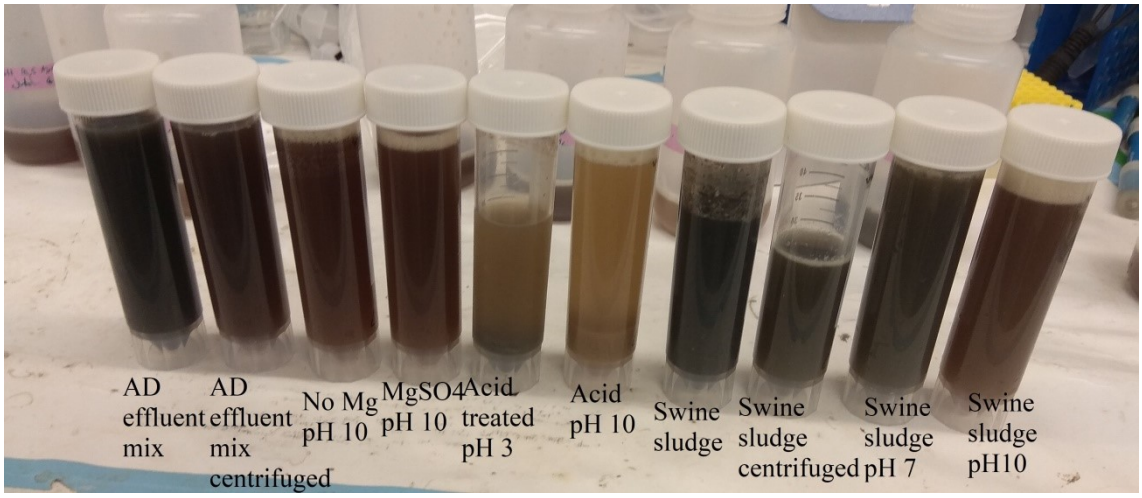


Figure 29. *Precipitation solutions of other experiments after precipitation. From left to right: AD mix, AD mix centrifuged, No Mg pH10, MgSO4 pH10, Acid treated pH 3, Acid treated pH10, Swine sludge, Swine sludge centrifuged, Swine sludge pH 7, and Swine sludge pH 10.*

Colour of the liquid was changed increasingly with pH level from 8 to 11.5 level indicating that phosphorus removal wasn't main reason for colour change, but pH level of the precipitation solution.

Other experiments precipitation solution colour change was very similar as in pH series batches. Without magnesium and $MgSO_4$ batches colour was close to pH 10 batch. Colour changed drastically with acid treated batch at pH 3 level. Acid treated batch at pH 10 has colour close to pH 3 but more precipitants settled at the bottom. Swine manure batches had similar changes in colour as pH test. Colour changes from dark to lighter reddish at higher pH levels and might be caused by organic molecules or iron ions reacting new pH level.

Prepared crystals for XRD analysis showed similar colour in all experiment batches. All crystal samples had slight colour of reddish brown with small amount dark coloured pieces probably other organic solids from precipitation solution (Figure 30).

Figure 30. *Picture from dried and mixed precipitated crystals from acid treated batch on pH 10*

Precipitation colour might come from the colour of the precipitation solution. All of the precipitation solutions had slight brownish and reddish colour and it could have end up in the precipitated crystals. Also precipitated crystals were collected by centrifuge and dried, so some of the liquid and organic matter ended up with the crystals.

5.2.12 Economical evaluation of struvite precipitation

Economical evaluation of the struvite precipitation is done using information gained from the experiments. Only chemical costs to produce are evaluated, because other changing costs, such as operational costs, maintenance costs, building costs etc. are difficult to estimate and have variability (Yetilmezsoy et al. 2017). Costs of the used chemicals are described in Table 10.

Table 10. *Chemicals used in experiments, their prices and molar weights. (Yetilmezsoy et al. 2017)*

Chemical	Price ($) per ton	Molar weight (g/mol)
$MgCl_2 \cdot 6H_2O$	750	203.3
$MgSO_4 \cdot 7H_2O$	500	246.48
NaOH	500	40.01
H_2SO_4	200	98.08

Chemical costs for different experiments done are presented in Table 11. In the experiments, chemical amounts used for precipitation aren't necessarily optimal in economical sense, but to maximize precipitation and phosphorus removal. For example, lower amounts of magnesium substrates could have used for precipitation to decrease chemical costs, but costs weren't main focus in these experiments. Chemical costs could be decreased if crystallization is done using naturally available soluble cations, especially in acid treated method. Also it has to be noted, that not all of the precipitated phosphorus was crystallized to MAP, but also to other phosphates.

Table 11. *Phosphorus removal efficiencies, chemical components costs $/ton struvite, total costs of struvite, and phosphate rock equivalent cost of different experiments.*

Experiment	Phoshorus removal efficiency	$MgCl_2 \cdot 6H_2O$ $/ton struvite	$MgSO_4 \cdot 7H_2O$ $/ton struvite	NaOH $/ton struvite	H_2SO_4 $/ton struvite	Struvite $/ton	P_2O_5 $/ton
pH 8	80 %	1420	0	0	0	1420	4909
pH 10	92 %	1228	0	16109	0	17336	59951
pH 10 No Mg	51 %	0	0	29349	0	29349	101493
pH 10 $MgSO_4$	86 %	0	1068	17337	0	18405	63648
Swine pH 7	80 %	1699	0	0	0	1699	5875
Swine pH 10	98 %	1397	0	9773	0	11170	38627
Acid treated pH 10	99 %	737	0	913	1053	2703	9346

Calculated costs indicate that adjusting pH with NaOH isn't economical and will increase costs radically, even though it can provide better removal efficiency of phosphorus. Magnesium substrate addition increases costs significantly, but these costs

could be potentially decreased using cheap magnesium substrates, such as wood ash or seawater. Acid treatment method is relatively inexpensive way to produce struvite and other phosphates and is possible, because acid treatment decreases effluent buffer capacity and increasing pH from 3 to 10 consumes as much of NaOH as pH 10 experiment. Acid treated method could be also more inexpensive if only soluble cations were used and pH was adjusted to level 5 and increased lower pH level, even though it could affect on phosphorus removal efficiency.

Market price of the struvite is variable depending on the use and application requirements. Selecting right price for struvite is important for economic analysis of profitability. Market sale price for struvite needs to be higher than total expenses of fertilizer production, which include chemical costs and production facility costs. Therefore suitable sale price must be estimated. Dirk (2009) estimated price for struvite fertilizers would range from $365 to $1480 per ton. Stamatelatou & Konstantinos (2015) estimated that based on nitrogen and phosphorus content struvite fertilizer price would be around $234/ton and market price for phosphate rock (P_2O_5) about 100$/ton. All of the experiments had high chemical costs, especially when pH was adjusted with NaOH.

6. CONCLUSIONS

The optimal pH for precipitate phosphorus was found to be in range of 9.5-10.5, on the other hand pH levels of 8.5 and 9 were found to be about 4% less efficient, but consuming much less NaOH. Precipitation time wasn't observed to affect on precipitation efficiency after one day possible reaching equilibrium in solution, but more research is needed to confirm the observation. Magnesium substrate type was observed to have no significant difference, at least on studied $MgCl_2$ and $MgSO_4$. However, without magnesium addition phosphorus removal efficiency in pH 10 decreases significantly from 92% to 51%. Swine manure phosphorus removal was successful in original pH 7 and pH 10 level with efficiencies of 80% and 98%. Swine manure had also higher starting concentration of phosphorus and cations compared to effluent, which could explain high removal efficiency.

Phosphorus can be released from the digestate by lowering the pH with acid treatment method. Digestate solids consists about 93% of the available phosphorus. Most of the phosphorus was released between pH 7 and 6. Lower pH levels released less phosphorus. Released phosphorus can be effectively removed by precipitation after magnesium addition and pH level increase. Almost all of the released phosphorus was successfully removed (99%) by precipitation.

Cation concertation analysis showed that magnesium levels decreased more than phosphorus levels in most of the experiments and could indicate that some of the magnesium is consumed to other precipitants than phosphates. Also calcium concentration levels were decreased after precipitation, most likely due to the precipitation of phosphates and carbonates. XRD-analysis suggested that phosphorus is precipitated as MAP-struvite but also K-struvite. Significant part of the phosphorus is also precipitated as calcium phosphates in higher pH levels.

Struvite precipitation for fertilizer production isn't economical viable method when using conventional magnesium substrates. Cheaper magnesium sources could make struvite production affordable. Controlling pH is the most expensive factor when considering struvite fertilizer production. However, optimal chemical use wasn't studied and fertilizer production from struvite would need more research.

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APPENDIX A: ADDITIONAL SEM PICTURES

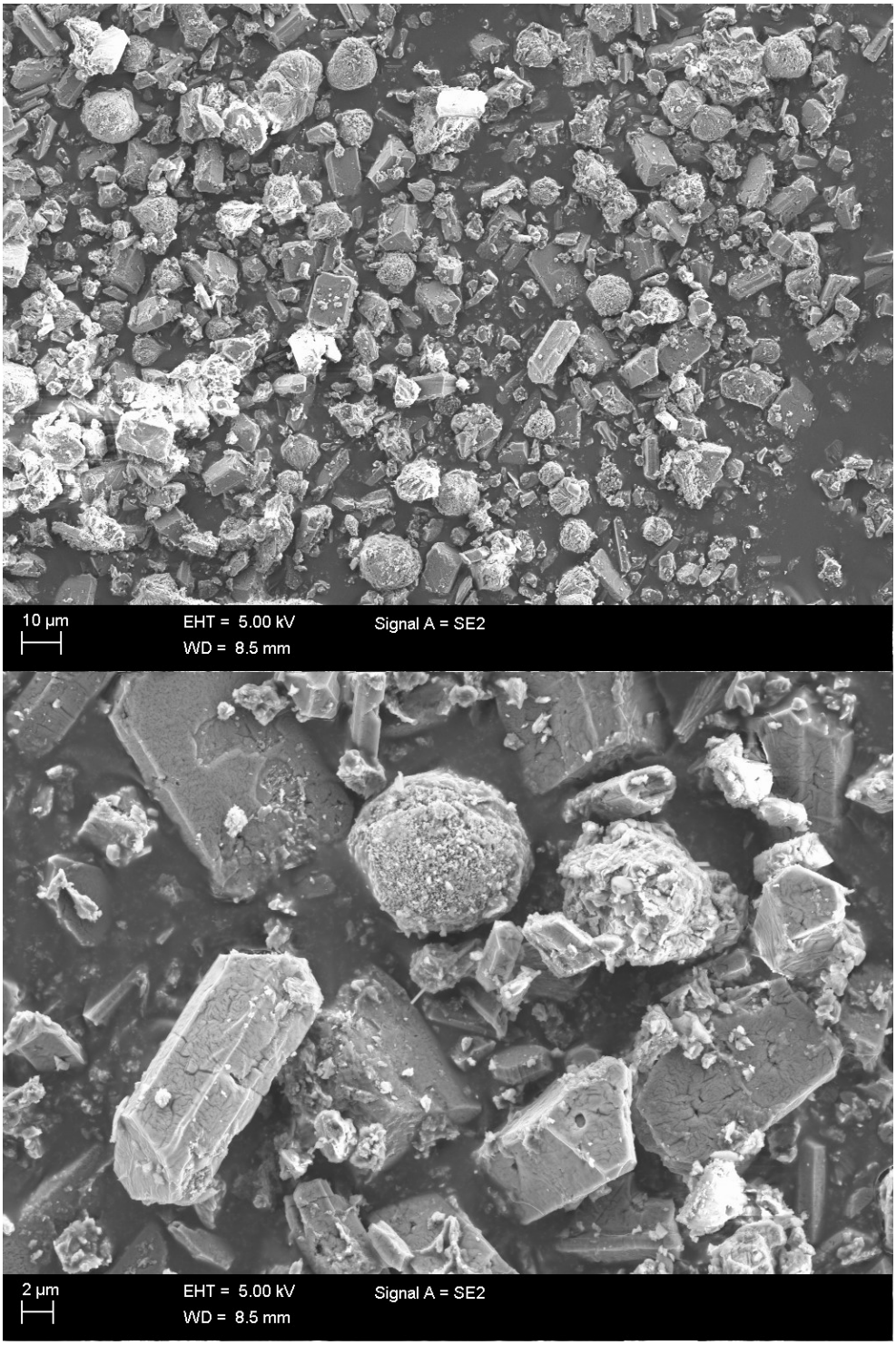

Figure 31. *SEM pictures from acid treated batch crystal sample*

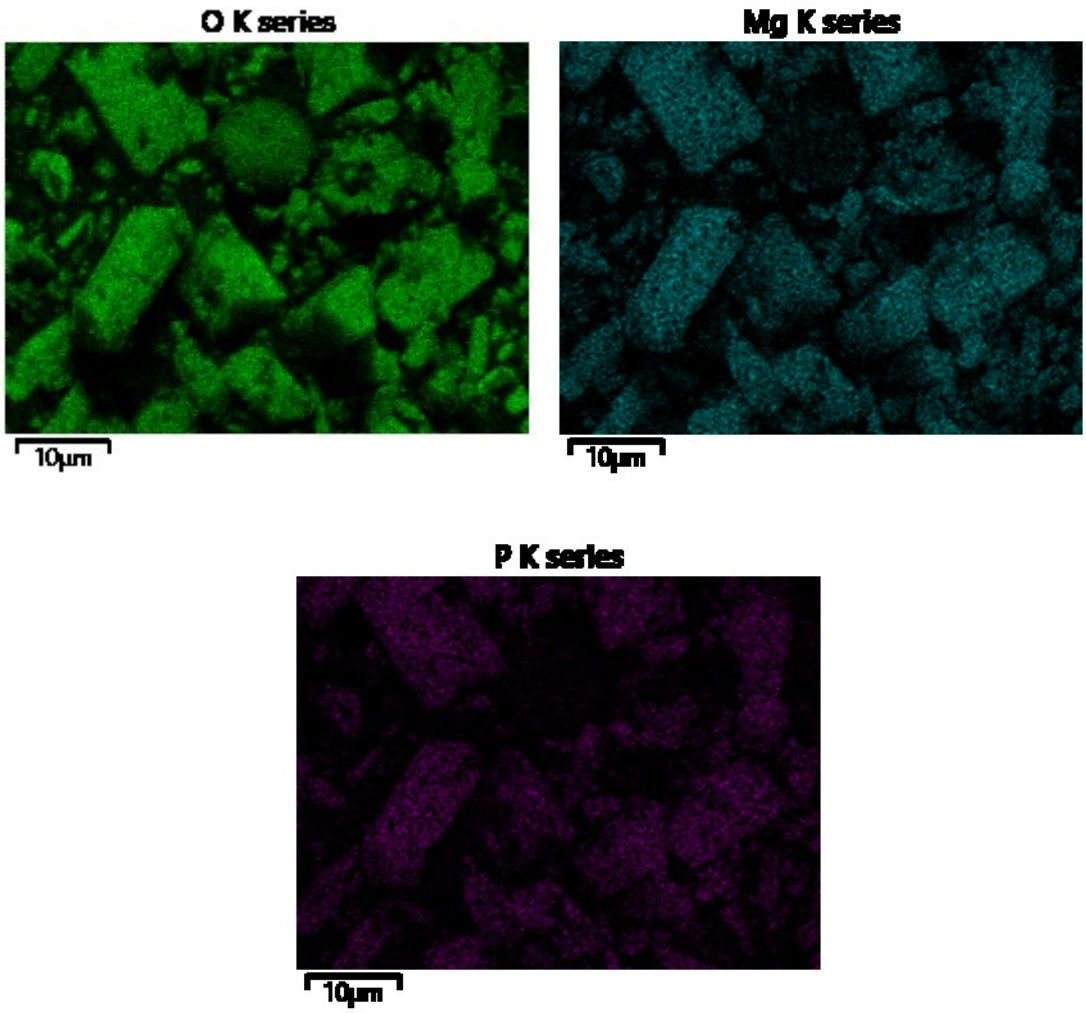

Figure 32. *SEM elemental analysis pictures of oxygen, magnesium and phosphorus from acid treated batch crystal sample*